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FRANK J. SEILER RESEARCH LABORATORY

CONDENSED PHASE KINETIC

DEUTERIUM ISOTOPE EFFECTS

IN HIGH ENERGY PHENOMENA:

MECHANISTIC INVESTIGATIONS

AND RELATIONSHIPS

SCOTT A. SHACKELFORD

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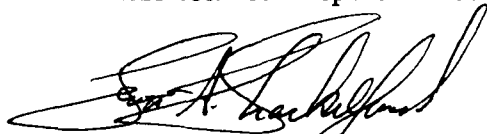
This document was prepared by the Energetics and Properties Research Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO and was written under the auspices of Project Work Unit 2303-F3-05, Energetic Materials Reactivity and Structure. It reviews the use of condensed phase kinetic deuterium isotope effects (KDIE) for determining an energetic material's rate-controlling step during the thermochemical decomposition process, plus the extension of this KDIE approach at other DOD and DOE laboratories into higher order energetic pyrolysis, combustion, thermal explosion, and detonation phenomena using TNT, TATB, HMX, and RDX. As Work Unit Chief, Major (then Capt) Scott A. Shackelford conceived the original liquid TNT and HNBB thermochemical decomposition KDIE research conducted at this laboratory; subsequently, he initiated similar KDIE decomposition and combustion investigations with HMX and RDX at the Astronautics Laboratory, Edwards AFB, CA.

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16. Nitramines
17. Initiation
18. Thermal Decomposition
19. Deuterium Compounds
20. HMX
21. RDX
22. TATB
23. TNT
24. HNBB

## PREFACE

This report contains two written tutorial lectures of 35 presented at the NATO Advanced Study Institute on "Chemistry and Physics of the Molecular Processes in Energetic Materials" held 3-15 Sep 1989 at Altavilla Milicia (Sicily) Italy. These two particular lectures review the use of the condensed phase kinetic deuterium isotope effect (KDIE) approach for determining, *in situ*, the key mechanistic features which control the energy releasing characteristics of various high energy phenomena displayed by the energetic materials, TNT, HNBB, TATB, RDX, and HMX. Lecture one describes the KDIE mechanistic investigations which reveal the rate-controlling mechanistic steps found in the thermochemical decomposition process for these pure energetic materials. Lecture two addresses mechanistic relationships determined by the extension of this condensed phase KDIE mechanistic approach into progressively more drastic high temperature/pressure/rate regimes exemplified by the rapid pyrolysis process, plus combustion, thermal explosion, and detonation events. The author wishes to acknowledge partial travel support by this NATO Advanced Study Institute in order to present these two lectures.

Dr Surya N. Bulusu served as Director of this NATO Advanced Study Institute and is Editor of an upcoming proceedings containing all 35 written lectures presented at the institute. These lectures were prepared by 21 research scientists from seven countries, active in the respective fields they reviewed. In total, these lectures represent an interdisciplinary compilation of the most recent advances of a state-of-the-art fundamental understanding for conventional energetic material behavior. The NATO ASI proceedings containing these 35 written lectures is scheduled for publication in the Spring of 1990 by Kluwer Academic Publishers. Those interested in obtaining a copy of these NATO ASI proceedings on "Chemistry and Physics of the Molecular Processes in Energetic Materials", may contact the publisher or editor:

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## SUMMARY

### MECHANISTIC INVESTIGATIONS OF CONDENSED PHASE ENERGETIC MATERIAL DECOMPOSITION PROCESSES USING THE KINETIC DEUTERIUM ISOTOPE EFFECT

The condensed phase kinetic deuterium isotope effect (KDIE) approach directly reveals the rate-controlling mechanistic step that ultimately determines the rate at which energy is released by an energetic material's thermochemical decomposition process. This paper reviews the KDIE concept and discusses previous condensed phase KDIE mechanistic investigations conducted during the thermochemical decomposition process of various nitroaromatic (TNT, HNBB, TATB) and nitramine (HMX, RDX) compounds using isothermal DSC and TGA analyses. Isothermal DSC evaluation methods used for obtaining an energetic compound's KDIE and in determining its rate-controlling step are outlined, and the possible dependence of the rate-limiting step on an energetic compound's physical state during the thermochemical decomposition process is considered.

### MECHANISTIC RELATIONSHIPS OF THE DECOMPOSITION PROCESS TO COMBUSTION AND EXPLOSION EVENTS FROM KINETIC DEUTERIUM ISOTOPE EFFECT INVESTIGATIONS

The condensed phase kinetic deuterium isotope effect (KDIE) approach directly determines the overall rate-controlling mechanistic step of an energetic material's complex thermochemical decomposition process. This second paper discusses extending the KDIE approach into progressively more drastic high temperature/pressure/rate regimes encountered with pyrolytic decomposition/deflagration, combustion, thermal explosion, and detonation incidents in order to determine the rate-controlling step of each. This rate-controlling step provides a common basis for comparing the mechanistic similarities or differences among these high energy incidents; and possible relationships between the thermochemical decomposition process and higher order combustion or explosion incidents are described for HMX, RDX, TATB, and TNT. The KDIE determined rate-controlling step between a pure nitramine compound and a formulated energetic material also is compared.



# MECHANISTIC INVESTIGATIONS OF CONDENSED PHASE ENERGETIC MATERIAL DECOMPOSITION PROCESSES USING THE KINETIC DEUTERIUM ISOTOPE EFFECT

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**ABSTRACT.** The condensed phase kinetic deuterium isotope effect (KDIE) approach directly reveals the rate-controlling mechanistic step that ultimately determines the rate at which energy is released by an energetic material's thermochemical decomposition process. This paper reviews the KDIE concept and discusses previous condensed phase KDIE mechanistic investigations conducted during the thermochemical decomposition process of various nitroaromatic (TNT, HNBB, TATB) and nitramine (HMX, RDX) compounds using isothermal DSC and TGA analyses. Isothermal DSC evaluation methods used for obtaining an energetic compound's KDIE and in determining its rate-controlling step are outlined, and the possible dependence of the rate-limiting step on an energetic compound's physical state during the thermochemical decomposition process is considered.

## 1. Introduction

Thermally initiated decomposition of an energetic material is an extremely complex process involving numerous sequential and parallel chemical reactions. Of all the chemical reactions contributing to the thermochemical decomposition process, one reaction will progress more slowly than all others. This slowest chemical reaction is perhaps the most important one taking place because it contains the rate-controlling mechanistic step. It is this rate-controlling step that ultimately determines the overall rate at which an exothermic decomposition proceeds by kinetically regulating an energetic compound's rate of energy release. By using the kinetic deuterium isotope effect (KDIE) approach, this slow rate-controlling step is selectively identified during the thermochemical decomposition itself, despite the presence of the numerous other participating chemical reactions, and is observed only if the deuterium labeled site of a compound or a position in the near vicinity of the deuterium atom, participates in the slowest chemical reaction's rate-controlling step along a given mechanistic pathway. The KDIE is observed by comparing differences in reaction rates between a normal hydrogen atom containing energetic compound and this same compound's isotopically substituted deuterium analogue.

Although mainly used in more easily defined gas phase and solvolyzed

chemical reaction systems, application of the KDIE approach to neat condensed phase (solid, mixed melt, liquid) energetic compounds permits the direct, non-intrusive, in-situ identification of the rate-controlling mechanistic step during the thermochemical decomposition process itself. Sometimes also referred to as the rate-determining step or rate-limiting step, the mechanistic rate-controlling step results from the dissociation of chemical bonds or attractive interactions; but, it is necessary to realize in the case of a chemical bond rupture, that the rate-controlling mechanistic step may not be the first chemical bond dissociation to occur along a given mechanistic pathway. The first chemical bond rupture in an energetic compound may affect the specific mechanistic pathway a decomposition process will follow; however, the rate-controlling chemical bond rupture occurs somewhere along the mechanistic pathway and determines the energy release rate and overall velocity of the thermochemical decomposition process. Condensed phase KDIE investigations of various energetic materials selectively reveal two new mechanistic insights about the thermochemical decomposition process. First, the rate-controlling step can be dependent upon an energetic compound's predominant physical state; and secondly, extension of condensed phase KDIE investigations into more hostile high energy incidents suggest the thermochemical decomposition process can mirror the mechanistic rate-controlling steps present in more drastic rapid pyrolytic decomposition/deflagration, combustion, thermal explosion, and detonation incidents.

This paper addresses the concept of the KDIE itself and outlines the use of the condensed phase KDIE approach for determining the mechanistic rate-controlling step in thermochemical decomposition process of various energetic compounds and their deuterium labeled analogues. Instrumental methods employed and isothermal DSC data evaluation techniques used with these condensed phase KDIE mechanistic investigations are also discussed. The second companion paper, "Mechanistic Relationships of the Decomposition Process to Combustion and Explosion Events from Kinetic Deuterium Isotope Effect Investigations," reviews extensions of the condensed phase KDIE into more hostile higher pressure/temperature/rate incidents wherein mechanistic comparisons can be made with the thermochemical decomposition process using the KDIE determined rate-controlling step as a common experimental parameter.

## 2. Discussion

### 2.1 KINETIC DEUTERIUM ISOTOPE EFFECT (KDIE) CONCEPT

When a normal hydrogen atom is replaced by a heavier deuterium atom in a given chemical compound, a difference in reaction rate is observed if the newly labeled chemical bond, or a bond in the near vicinity, ruptures during the slowest chemical reaction step. This rate variation between the normal and deuterium labeled compound originates from the difference in ground state or zero-point vibrational energy between a compound's carbon-hydrogen (C-H) and identical but stronger carbon-deuterium (C-D) bond as illustrated by the normal HMX and perdeuterio-substituted HMX-d<sub>8</sub> chemical structures (Figure 1). Note the C-D bond has a lower zero-point vibrational energy level than the analogous C-H bond; this zero-point vibrational energy difference at approximately 2.3

Kcal/mol<sup>1</sup>, is a direct consequence of the deuterium atom's higher mass compared to the lighter hydrogen isotope.<sup>2,3</sup> During a single stepwise chemical reaction, or during a chemical reaction that is one of many sequential reactions during a complex chemical process, dissociation or rupture of the lower energy C-D bond proceeds in a less facile manner than its analogous higher energy C-H bond. Because the C-D bond initially begins at a 2.3 Kcal/mol lower zero-point vibrational energy, it requires a higher energy of activation to reach the reaction's transition state; this results in a slower reaction rate ( $k_d$ ) for the deuterium labeled compound so that  $k_h/k_d$  defines a KDIE greater than one.

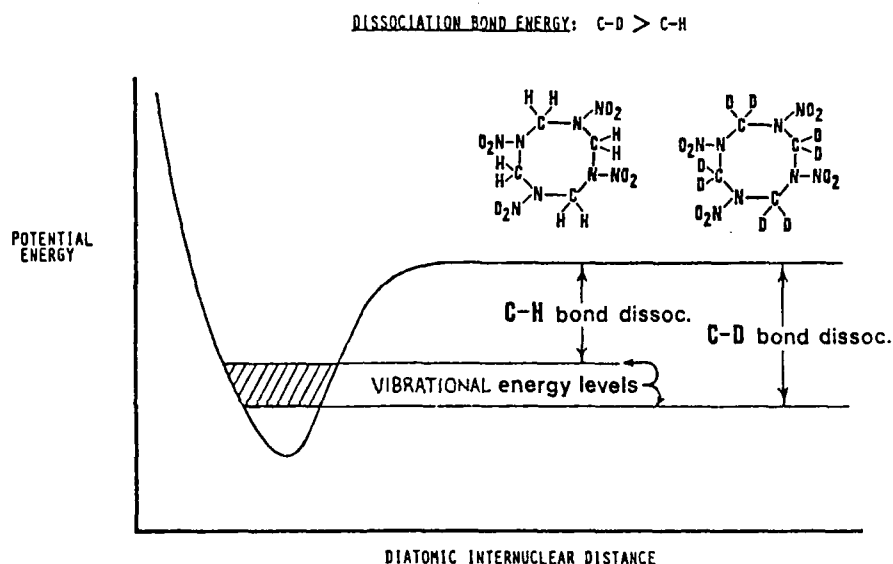


Figure 1. Potential energy curve for the C-H and C-D bond with HMX and HMX-d<sub>8</sub> chemical structures.

The KDIE value normally is expressed as a ratio between reaction rate constants of the normal C-H compound and its C-D labeled analogue. While  $k_h/k_d$  rate constants are most often used, inverse induction period times  $t_d/t_h$ <sup>5,6</sup> critical temperature  $T_{ch}/T_{cd}$ <sup>6,7</sup> burn rates  $r_{bh}/r_{bd}$ <sup>8</sup>, and impact sensitivity  $V_d/V_h$ <sup>9,10</sup> can be used since they all are dependent upon the global decomposition rate of the given energetic compound. This is especially important in chemical reactions or processes when one cannot directly obtain an experimental rate constant ( $k$ ).<sup>5,7-10</sup> There are three characteristics regarding the KDIE which one must remember, especially as it might apply to the complex thermochemical decomposition process of an energetic material:

(1) A KDIE is observed only during the slowest step in a given chemical reaction; or in the slowest chemical reaction of a multi-reaction process; therefore, a KDIE defines the rate-controlling step of a chemical reaction or process;

(2) The rate-controlling step may not be the first step in a chemical reaction sequence or mechanistic pathway; but, the rate-controlling step is often mistakenly assumed to be the initial step;

(3) The magnitude of the KDIE generally decreases with increasing reaction temperature; KDIE values ranging from 2.5 to 8 are normally seen at standard temperature.<sup>1, 3, 11</sup>

There are three types of KDIE possible, and these are illustrated using the HMX molecular structure (Figure 2). Direct C-H/C-D bond rupture during the rate-controlling step produces a primary (1°) KDIE where the ratio of HMX/HMX-d<sub>8</sub> rate differences would give a value greater than the theoretically minimum 1.41 value at an infinitely high temperature limit<sup>2</sup>; however, a value of 1.35 is an acceptable experimental lower limit for a 1° KDIE.<sup>3, 12-14</sup> Rupture of either bond adjacent to the C-H/C-D bond or one bond further away respectively provides an alpha or beta secondary (2°) KDIE whose values theoretically could lie between 1.01 and 1.34. Normally  $\alpha$  2° KDIE values range

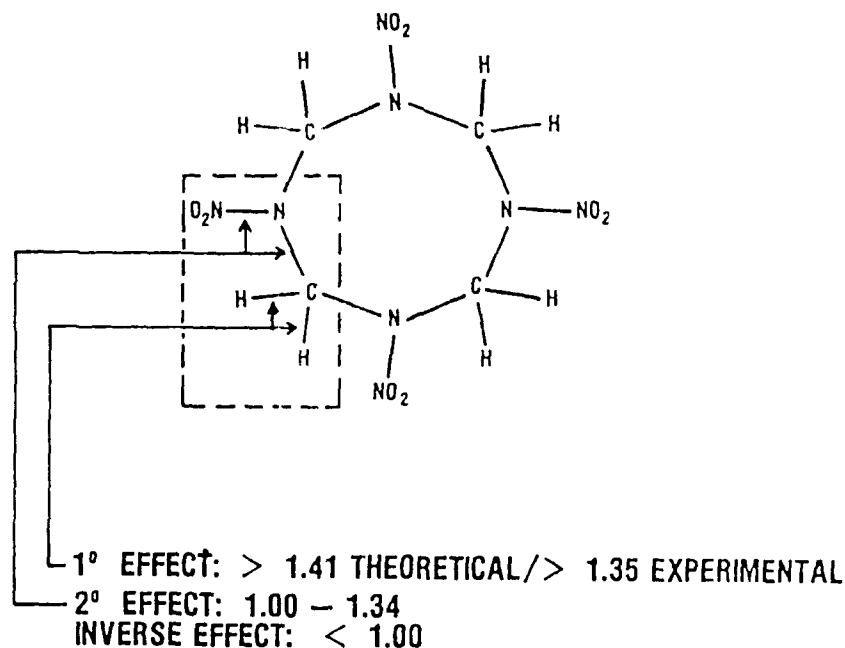


Figure 2. Possible KDIE types illustrated with the HMX chemical structure or structural fragment.

from 1.15 to 1.25 at standard temperature (298K) while  $\beta$  2° KDIE values stay around a 1.1 ratio.<sup>3</sup> The minimum infinitely high temperature value for a 2° KDIE would be one (1.00).<sup>3, 4</sup> Collectively, the 1° KDIE and 2° KDIE are sometimes referred to as normal or positive isotope effects because their magnitudes are greater than one (1.00). Finally, a third type of KDIE can occur where a KDIE value less than 1.00 indicates an inverse KDIE (*i*-KDIE). While the theory describing KDIE behavior can be quite complex; generally, both 1° and 2° KDIE values decrease with higher reaction temperatures<sup>2-4</sup> when the

rate-controlling step involves a covalent bond dissociation or rupture proceeding through in a fairly linear transition state<sup>2,10,15</sup>. The condensed phase KDIE investigations described for energetic material thermochemical decomposition differ greatly from more traditional mechanistic KDIE investigations in two main respects. First, much higher temperatures are encountered; and secondly, the energetic compounds react in the complex multi-reaction condensed phase process rather than under simpler, more easily controlled solvolyzed or gas phase reaction conditions. Application of the condensed phase KDIE to the high temperature thermochemical decomposition process occurs in a much more hostile chemical environment; and, in this respect, reaches into a new relatively unexplored experimental regime.

## 2.2 NITROAROMATIC CONDENSED PHASE KDIE STUDIES

The first mechanistic application of the condensed phase KDIE approach to the thermochemical decomposition of an energetic material was conducted with liquid 2,4,6-trinitrotoluene (TNT) and its  $\alpha$ ,  $\alpha$ ,  $\alpha$ -trideuteriomethyl labeled analogue (TNT- $d_3$ ) using isothermal differential scanning calorimetry (IDSC) analysis. This study revealed the first direct experimental evidence that covalent

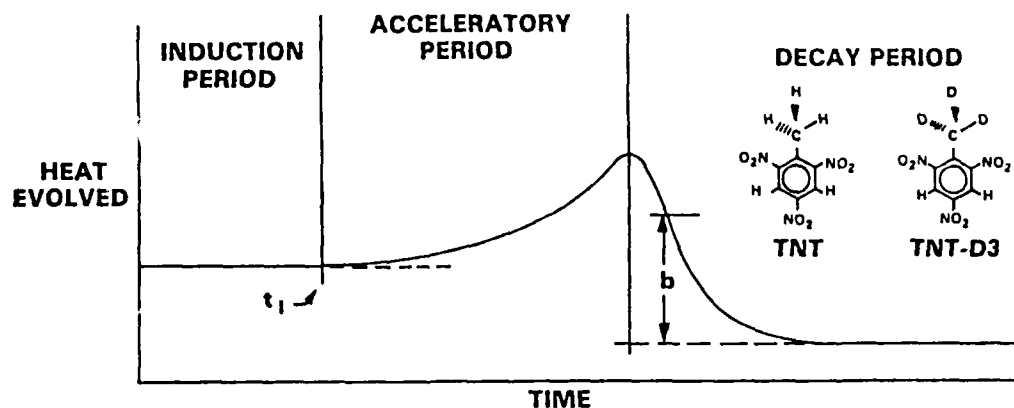


Figure 3. Generalized isothermal DSC curve for either the liquid TNT or liquid TNT- $d_3$  thermochemical decomposition process.<sup>5</sup>

homolytic C-H bond rupture in the TNT methyl group constitutes the rate-controlling step of its thermochemical decomposition process.<sup>5</sup> Figure 3 displays a generalized IDSC curve for the TNT thermochemical decomposition in which the heat evolved (y-axis) is measured against time (x-axis) at constant temperature. Because this ambient pressure liquid phase decomposition (mp TNT = 81–82°C) follows pseudo first order kinetics, the IDSC curve's deflection height (b) above the base line at any given time (t) is directly proportional to the rate of TNT heat energy evolution, which in turn, is directly proportional to TNT's rate of reaction or rate of disappearance as TNT converts to other decomposition products. This means that  $\ln b = kt$  takes on the form of a first

order rate equation and shows that the rate constant of a TNT or TNT- $d_3$  decomposition can be obtained directly from a linear plot of  $\ln b$  vs time where the rate constant ( $-k$ ) is the slope of the line.<sup>16</sup> This simplified determination of rate constants by IDSC, however, is valid only in cases where a decomposition follows first order or pseudo first order kinetics.<sup>17</sup>

Following IDSC data analysis convention, the TNT and TNT- $d_3$  rate constants evaluated during the decay phase of the thermochemical decomposition process (Figure 3), provides an averaged  $k_h/k_d$  KDIE value of  $1.35 \pm 0.02$  at temperatures ranging from 245 – 269°C (518–542 K).<sup>5</sup> From this borderline 1° KDIE value, several important observations emerge. TNT forms mainly condensed phase decomposition products (Figure 4); these remain in the liquid melt phase and undergo further decomposition themselves<sup>18, 19</sup>. Some of these isolated products 5, 6, do not involve a potential rate-controlling C–H bond rupture. Because IDSC measures the total rate of all contributing chemical

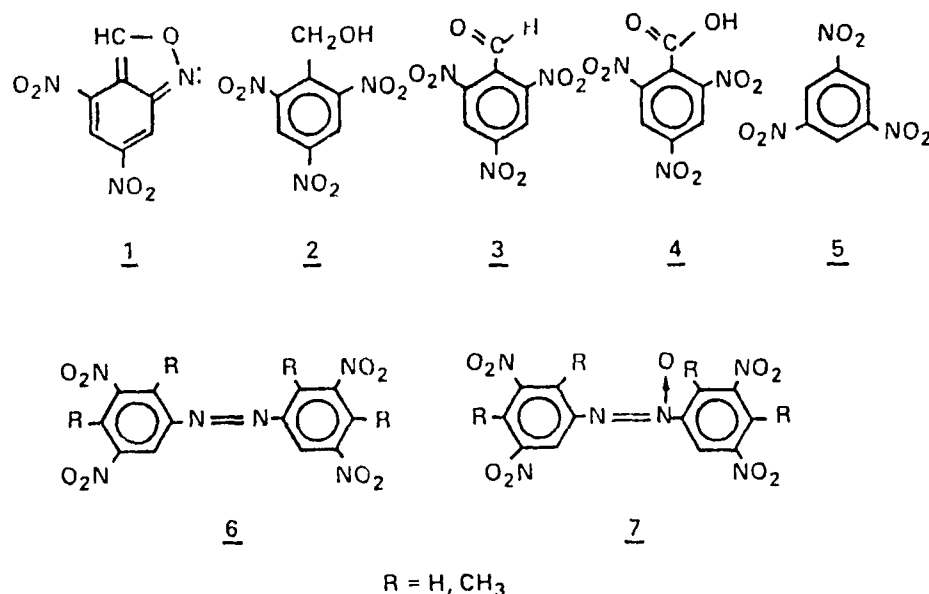


Figure 4. Isolated condensed phase products from the liquid TNT thermochemical decomposition process.<sup>5, 18</sup>

reactions during the TNT decomposition process, and because those reactions not involving a rate-controlling C–H bond rupture would contribute a factored  $k_h/k_d$  KDIE ratio of 1.00 to the overall measured  $k_h/k_d$  KDIE of 1.35, the 1.35 KDIE value is diluted or masked from its true higher value.<sup>5</sup> Therefore, the TNT rate-controlling step is detected earlier in the decomposition process before other subsequent condensed phase reactions could interfere with the true KDIE value. This early detection is justified by two other observations. First, a high pressure liquid chromatography (HPLC) analysis of TNT samples quenched during the seemingly innocuous induction period (Figure 3), reveals trace level formation of a new compound I from TNT. Secondly, when this unidentified

trace compound I is combined with a fresh TNT sample, it catalyzes TNT's autocatalytic decomposition and reduces the induction period ( $t_i$ ) nearly 2.5 times.<sup>5</sup> Condensed phase KDIE evaluation of the early induction period cannot be done using  $k_h/k_d$  rate constants because rate constants must be evaluated from the IDSC curve's baseline deflection represented by the height of  $b$  (Figure 3). The horizontal induction period generates no measureable deflection; however, induction times ( $t_i$ ) can be used and are conveniently measured from the IDSC curve.<sup>5</sup> The  $t_i$  value even can be used to determine the energy of activation ( $E_{a_i}$ ) for formation of the catalytic unidentified compound I.<sup>20</sup> Two mathematical approximations are invoked to provide equation 1 where  $k$  is the rate constant and  $i_i$  the small mole fraction of compound I formed at any given induction time,  $t_i$ .<sup>20</sup> Equation 2 represents the natural logarithmic form of the Arrhenius

$$k = i_i / t_i \quad (1)$$

equation, and equation 3 results from setting equation 2 equal to equation 1's logarithmic form. Equation 3 serves as the starting point for determining TNT's KDIE using induction times of TNT ( $t_{ih}$ ) and TNT- $d_3$  ( $t_{id}$ ). Equation 3 is

$$\ln k = E_{a_i} / RT + \ln Z \quad (2)$$

$$\ln k = \ln i_i - \ln t_i = E_{a_i} / RT + \ln Z \quad (3)$$

rearranged to give equation 4. Assuming the mole fraction ( $i_i$ ) of compound I must reach a specific threshold concentration<sup>21</sup> during the induction period

$$\ln i_i = \ln k + \ln t_i \quad (4)$$

( $t_i$ ) in order to catalyze TNT's thermochemical decomposition process into its exothermic acceleratory phase (Figure 3), only  $t_i$  and  $k$  may vary between the normal TNT compound and deuterium labeled TNT- $d_3$  during the decomposition process. Because  $i_i$  reaches a constant threshold concentration,<sup>5, 21</sup> equation 5 can be written from equation 4, and then simplifies into equation 6, to finally provide equation 7. Equation 7 establishes the necessary relationship between

$$\ln k_h + \ln t_{ih} = \ln i_i = \ln k_d + \ln t_{id} \quad (5)$$

constant

$$\ln k_h + \ln t_{ih} = \ln k_d + \ln t_{id} \quad (6)$$

$$\frac{k_h}{k_d} = \frac{t_{id}}{t_{ih}} \quad (7)$$

the  $k_h/k_d$  rate constant ratio and inverse  $t_{id}/t_{ih}$  induction time ratio for determining the induction period's KDIE, where a chemical reaction proceeds, but at a small enough extent that its heat release is not detected.<sup>5</sup> The inverse relationship exhibited by equation 7 makes sense when one notes that a larger rate constant ( $k_h$ ) represents a faster chemical reaction with a smaller (shorter) induction time ( $t_{ih}$ ).

A 1° KDIE equal to 1.66 results during the induction time portion of the TNT thermochemical decomposition process. This 1° KDIE value reveals covalent C-H bond rupture in TNT's methyl group is the rate-controlling step; and ultimately, this rate-controlling C-H bond dissociation determines the rate at which the entire exothermic TNT decomposition proceeds and releases its energy.<sup>5</sup> Most importantly, the induction period KDIE comes only from the decomposition of TNT itself. Further verification comes from a proton nmr analysis of a TNT sample quenched at the maximum energy output of the IDSC curve where the acceleratory phase ends and the decay phase begins. Although only 64% of the total heat was released at this point, 97% of the original TNT is consumed.<sup>22</sup> The remaining melt is primarily condensed phase TNT products undergoing further decomposition themselves to form more products during the decay phase (Figure 4). In this case, the decay phase  $k_h/k_d$  KDIE and its associated kinetics have little to say about decomposition of TNT itself since most of the TNT is reacted by the time the decay phase of the IDSC curve begins. A study of hydrogen atom versus ionic proton donation to the TNT molecule using hydroquinone and benzoic acid respectively, suggests the TNT methyl group C-H bond rupture is homolytic, involving transfer of a hydrogen atom since a 2% mixture of hydrogen atom donating hydroquinone reduces the induction time to zero, while proton donating benzoic acid has little affect.<sup>5</sup> Further verification of homolytic C-H bond rupture is found in electron spin resonance (epr) investigations.<sup>23-25</sup>

The thermochemical decomposition of TNT is controlled by a homolytic, covalent C-H bond rupture in its methyl moiety, and this rate-controlling step occurs very early in its overall thermochemical decomposition process. An intramolecular transfer of a hydrogen atom via the rate-controlling C-H bond rupture to the ortho-nitro group followed by the elimination of H<sub>2</sub>O, would provide the isolated 4,6-dinitroanthranil product **1** (Figure 4). An intermolecular hydrogen atom transfer from one TNT molecule during this rate-controlling C-H bond dissociation step would provide a 2,4,6-trinitrobenzyl radical and protonated TNT radical wherein the para-nitro group<sup>24</sup> picks up the hydrogen atom (Figure 5). An intermolecular coupling of these two radical species could produce the epr observed 3',5'-dinitro-4'-methyl-2,4,6-trinitrobenzyl nitroxyl radical **9**<sup>24, 25</sup> (Figure 5) via radical OH elimination, or possibly via the analogous benzyl oxonitroxyl radical **8** which readily converts to the nitroxyl radical at the temperatures needed for the thermally initiated TNT decomposition<sup>26</sup>. Further reaction of the nitroxyl radical by oxidative cleavage, continued reaction by the 4,6-dinitroanthranil, or progressive oxidation of the trinitrobenzyl radical itself, could produce the other monoaryl products previously isolated and characterized (Figure 4).<sup>18, 19</sup> Several concepts emerge from this TNT condensed phase KDIE mechanistic investigation that have a general applicability to the thermochemical decomposition process. First, a KDIE can be detected during the complex high temperature thermochemical decomposition process and identifies the specific mechanistic feature that ultimately constitutes the overall process's rate-controlling step. Secondly, this rate-controlling step can occur very early in the thermochemical decomposition process and can involve a slow chemical reaction sequence that proceeds to a minor extent. In other words, the mechanistic rate-controlling step may not occur in the most obvious reaction proceeding to the greatest detectable percentage or extent. Thirdly, KDIE values can be determined by comparing experimental data of the normal and analogous



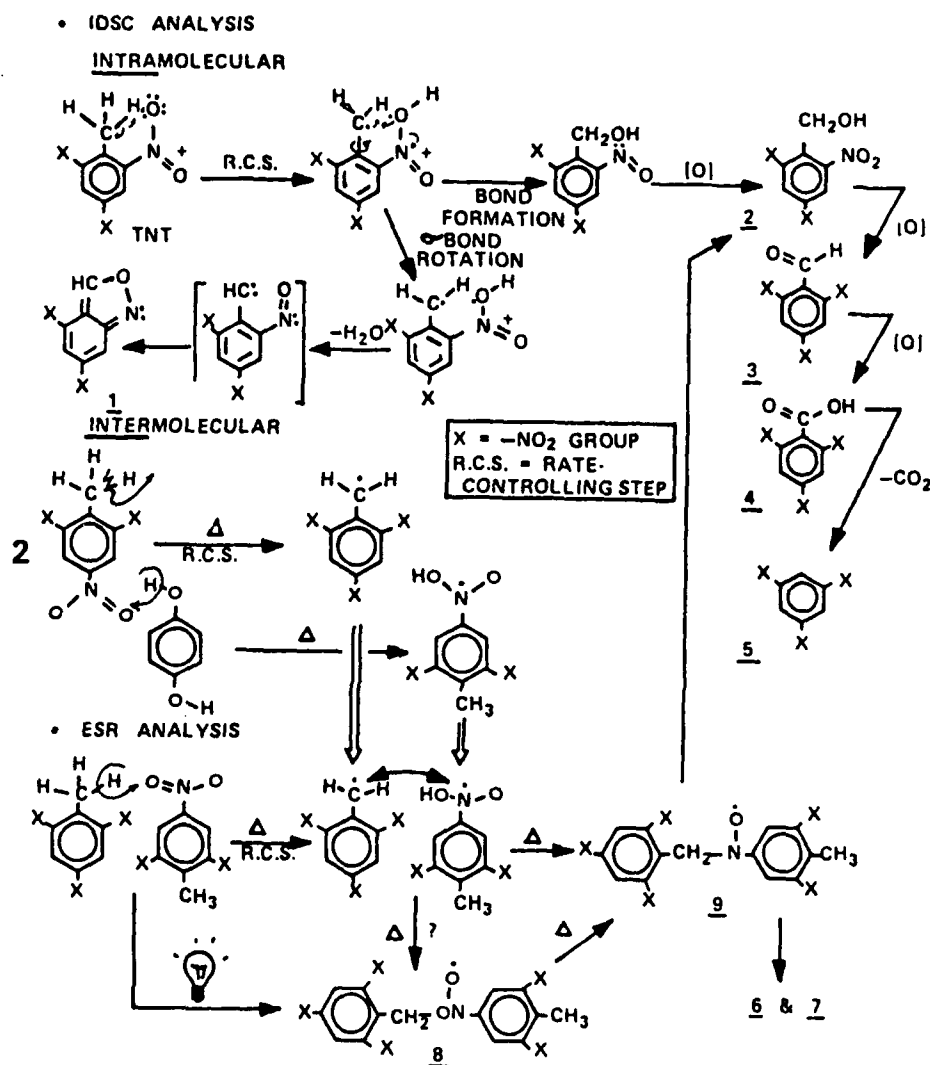


Figure 5. Possible mechanistic aspects of the liquid TNT thermochemical decomposition process.

deuterium labeled energetic compounds which are related to rate constants and reaction rates; that is, other comparative data like induction time ratios can be used in place of conventional rate constant ratios when rate constants cannot be obtained.

Finally, in cases where condensed phase products may be generated from the original decomposing compound, the early stage of the decomposition process is particularly important because further decomposition of these condensed phase products begins interfering with the decomposition reactions of the original compound under investigation; and, this can mask a true 1° KDIE even when it is present.

The compound, 2,2',4,4',6,6'-hexanitrobibenzyl (HNBB), is related in its molecular structure (Figure 6) to TNT, and displays a similar mechanistic behavior in its IDSC analysis. Liquid HNBB and HNBB-d<sub>4</sub> produced a 1° KDIE

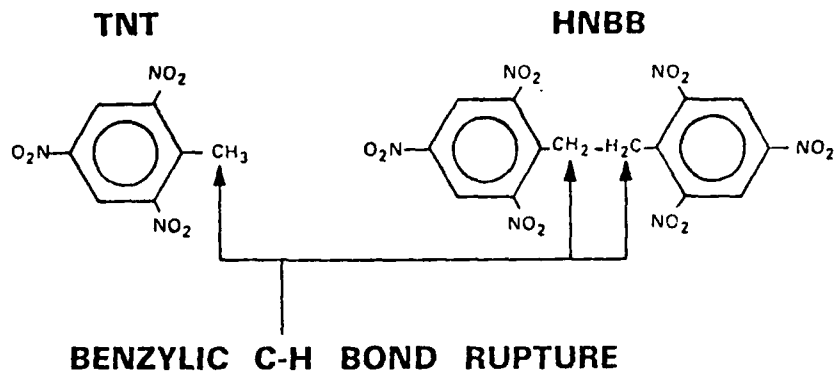


Figure 6. The chemical structures of TNT and HNBB.

equal to  $2.44 \pm 0.35$  during the induction period as well as from its decay phase ( $2.35 \pm 0.41$ ).<sup>27</sup> These 1° KDIE values appear over a 248–269°C temperature range and suggest covalent C–H bond rupture at the benzylic position constitutes the rate-controlling step in the liquid HNBB thermochemical decomposition process. This is the same structural position of TNT's rate-controlling C–H rupture.

The highly insensitive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and its deuterium labeled amino group analogue (TATB-d<sub>6</sub>) have also been studied by IDSC at ambient pressure in a 570–655K temperature range.<sup>6</sup> Because TATB decomposes in its solid state within this temperature range, a more complex thermochemical decomposition process is encountered (Figure 7). This complexity is reflected in its IDSC curve which displays two consecutive autocatalytic reaction sequences, each with its own maximum peak energy release.<sup>6, 22</sup> Pseudo first order kinetics are not unsuitable for evaluating this IDSC curve, and an autocatalytic rate plot (Figure 8) must be used where  $d\alpha/dt$  is plotted against  $\alpha(1-\alpha)$ , with  $\alpha$  representing the mole fraction of decomposed energetic material (TATB) at any given time (t).<sup>28</sup> The term  $\alpha$  is found as the progressive Simpson's Rule summation of  $\Delta\alpha/\Delta t$  (Figure 7) to provide the partial area (a) under the IDSC curve of TATB divided by the total area (A) or:

$$\alpha = \text{area at time } t / \text{total area} = a/A$$

Because the IDSC measures the total heat evolved by an energetic material, and because this heat evolution is proportional to the global rate at which an energetic material chemically reacts during its decomposition process, the overall

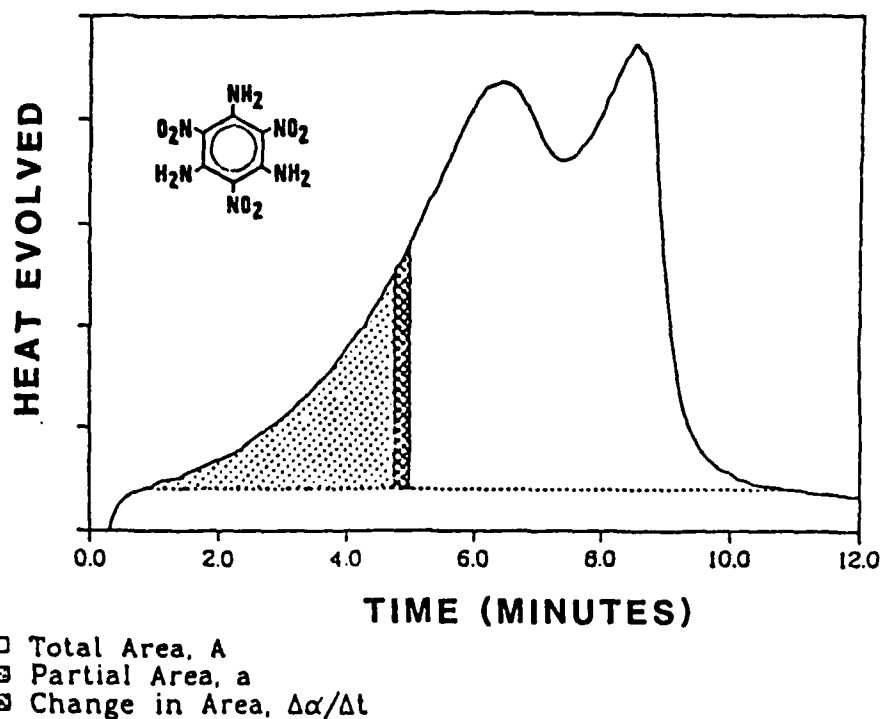


Figure 7. Isothermal DSC curve for either the solid state TATB or solid state TATB- $d_6$  thermochemical decomposition process<sup>6, 28</sup> with TATB and TATB- $d_6$  chemical structure.

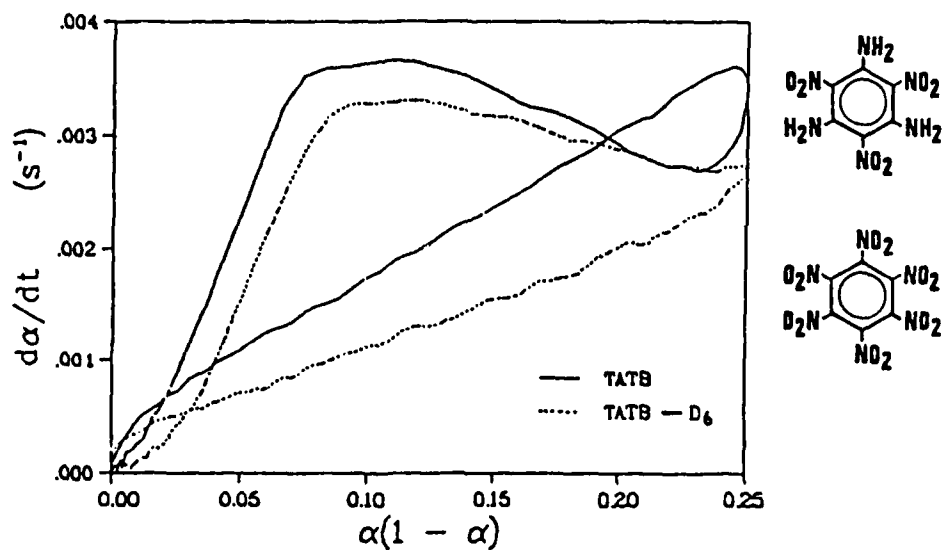


Figure 8. Folded autocatalytic rate plot for both the solid state TATB and the solid state TATB- $d_6$  thermochemical decomposition process. <sup>6, 28</sup>

rate of decomposition at any given time ( $t$ ) is described by the following approximation:  $d\alpha/dt = \text{height (h) above baseline at } t/\text{total area} = h @ t/A$ , because  $h$  is proportional to a very small  $\Delta\alpha/\Delta t$  segment,<sup>28</sup> especially if one chooses a very small  $\Delta t$  value. The autocatalytic rate plot (Figure 8) for TATB is based upon the specific rate equation<sup>6</sup> where the slope of any linear segment

$$d\alpha/dt = k\alpha(1 - \alpha) \quad (8)$$

provides the rate constant ( $k$ ). Two segments of linearity are seen in this type of rate plot where the curve folds back on itself at  $\alpha(1 - \alpha) = 0.25$ . The two linear segments define a consistent component reaction where a single mechanism likely predominates during the linear portion of the complex decomposition process. Further verification of a consistent mechanism in this portion of the IDSC curve would be achieved if this linear portion remains when separate isothermal IDSC decomposition runs are conducted over a wide temperature range.<sup>6</sup> An early linear segment occurs during the first autocatalytic solid state reaction sequence prior to reaching the first energy release maximum. This first linear segment displays a difference in slope between TATB and TATB- $d_8$  where  $k_h/k_d$  is about 1.5 and reveals a  $1^\circ$  KDIE.<sup>6</sup> The second linear segment occurs in the decay period of the second autocatalytic reaction sequence beyond the second energy release maximum and shows no TATB/TATB- $d_8$  slope difference ( $k_h/k_d = 1.00$ ), and no KDIE. The  $1^\circ$  KDIE suggests that solid state covalent N-H bond rupture in TATB's amino moiety constitutes the rate-controlling step early in its global thermochemical decomposition process. This finding is supported by elemental analysis showing the decomposed TATB residue is nearly devoid of hydrogen atoms during this final decomposition curve portion where no KDIE is observed.<sup>6</sup> More recent thin-layer chromatography (TLC) elution of the decomposed TATB, followed by chemical ionization mass spectral (CEMS) and x-ray photoelectron spectroscopy (XPS) analyses of the TATB decomposition products, reveal three compounds in which hydrogen atoms are lost.<sup>29</sup> These three furazan products apparently form by the loss of  $H_2O$  with cyclization of adjacent amino and nitro pendant groups (Figure 9). This loss of H atom by amino group again is consistent with the  $1^\circ$  KDIE and rate-controlling step N-H bond rupture found in the early portion of the solid state TATB decomposition process.

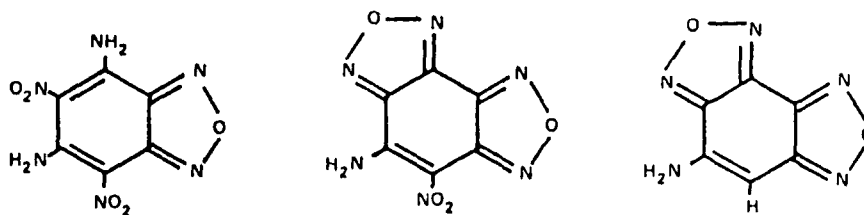


Figure 9. Isolated furazan products of the TATB thermochemical decomposition process showing loss of H atoms by N-H bond rupture.<sup>29</sup>

### 2.3 NITRAMINE CONDENSED PHASE KDIE STUDIES

The thermochemical decomposition process followed by the two most prominent nitramines, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and its six-membered cyclic analogue, hexahydro-1,3,5-trinitro-1,3,5-triazocine (RDX) is still not well understood and continues to be a matter of spirited mechanistic discussion. Recent condensed phase KDIE investigation of the HMX thermochemical decomposition process by IDSC possibly reveals one reason why.<sup>7</sup> An examination of the HMX molecular structure reveals several different positions where bond rupture during a rate-controlling step would provide a different type of KDIE (Figure 2). Indeed, when HMX and HMX-d<sub>8</sub> are investigated by IDSC, three dissimilar KDIE values are found over the entire decomposition process; and each occurs in a different physical state (Figure 10, top).<sup>7</sup>

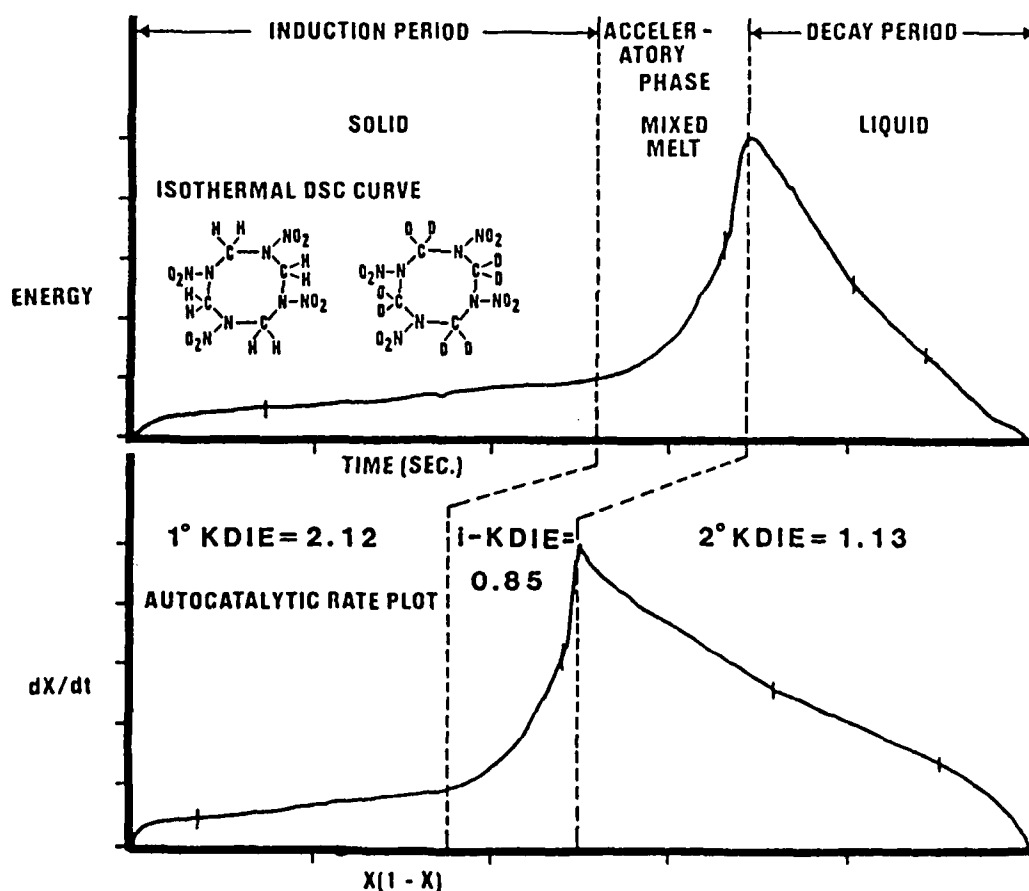


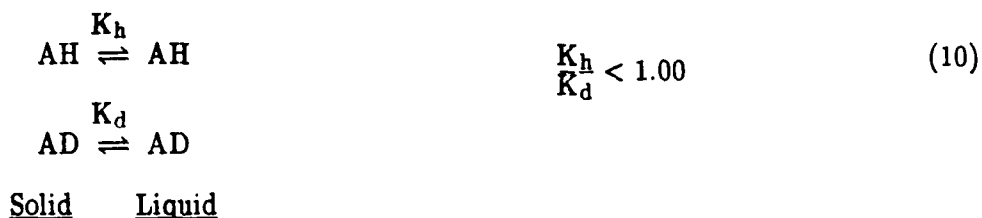
Figure 10. (TOP) Isothermal DSC curve of the HMX thermochemical decomposition process. (BOTTOM) Unfolded autocatalytic rate plot of the HMX thermochemical decomposition curve.<sup>7</sup>

Like TATB, the HMX thermochemical decomposition curve (Figure 10, top) fits an autocatalytic rate plot (Figure 10, bottom), which in this case is an unfolded representation. This unfolded autocatalytic rate plot [ $x = \alpha$  = the mole fraction of decomposed HMX at various times ( $t$ )] displays three linear segments that likely represent a consistent mechanistic feature for each. Like liquid TNT and HNBB, the HMX IDSC curve consists of an induction period, acceleratory phase, and decay period, but unlike, liquid TNT, HNBB, or solid TATB where the decomposition was investigated in one physical state, HMX decomposition progresses through three different physical states, each of which correlate with one of the linear autocatalytic rate plot segments. These three physical states were verified visually by observing liquid N<sub>2</sub> quenched IDSC samples with a microscope and with scanning electron microscope pictures. The induction period corresponds to solid state HMX decomposition and contains the first linear segment in the autocatalytic rate curve (Figure 10, bottom). Induction time ratios of HMX and HMX-d<sub>8</sub> over a 278–280°C (551–553K) temperature range (mp HMX = 282° C)<sup>30</sup> provide a  $t_{id}/t_{ih}$  equal to 2.12. This 2.12 KDIE value corresponds to a high temperature 1° KDIE and indicates that covalent C–H bond rupture is the rate-controlling step of solid state HMX decomposition.<sup>7</sup>

The acceleratory phase results when HMX begins melting and ends at the maximum point of heat energy release where the HMX sample is totally liquefied. The acceleratory phase exhibits a short linear segment just before the peak of its heat energy release, and the HMX/HMX-d<sub>8</sub> slopes of this linear segment exhibit a KDIE value less than one (0.85).<sup>7</sup> Because the KDIE results from force constant changes between the ground state and activated complex in a chemical reaction,<sup>31</sup> this inverse KDIE suggests the C–D bond's force constant is increasing at a faster rate than the C–H force constant as the highly oriented intermolecular crystal lattice forces are thermally overcome to produce liquefaction. Because the C–D with its heavier deuterium atom is already at a lower vibrational energy than its analogous C–H bond, one would expect the C–D bond would contract more readily as its force constant increases and provide the observed  $i$ -KDIE.<sup>7, 32</sup> Among the many attractions intermolecular in the HMX crystal lattice,<sup>33</sup> the inverse KDIE is specific only to its solid state intermolecular hydrogen bonds<sup>34</sup> and results from a shortening of the C–D or C–H bond as the highly oriented solid state intermolecular hydrogen bonds are thermally weakened.<sup>7</sup> From a qualitative viewpoint<sup>3</sup>, the heavier deuterium atom concentrates itself at a molecule's site where it is most strongly bonded and where its force constant is largest. In the case of an actual chemical reaction, the deuterium atom favors the reactant where the force constant is larger, while the higher energy hydrogen atom, relative to the deuterium atom, prefers the transition state where the force constant is lower. Therefore, the normal unlabeled compound will proceed faster through the chemical reaction to reach the transition state and give a positive KDIE. For an equilibrium reaction,<sup>3</sup> the deuterium isotope still prefers the situation where its more strongly bonded. If its force constant is higher in AD than in BD, the deuterium isotope prefers AD. Relative to its deuterium isotope, the hydrogen atom, however, prefers BH where force constants are lower, and  $K_h/d$  will be greater than one (positive KDIE).<sup>3</sup>



This same equilibrium reasoning applies to a melting organic compound. The portion of HMX or HMX- $d_8$  molecules not yet undergoing decomposition during liquifaction, would possess C-H or C-D bonds with higher force constants in the liquid phase where opposing intermolecular hydrogen bonding attractions would be weaker than in the rigid, highly ordered solid state crystal lattice.<sup>7</sup> In this situation, the force constant of the C-D bonds in AD would be higher in the liquid state from bond contraction than in the solid phase; but, because the heavier D atom concentrates itself where it is most strongly bonded, relative to the lighter H atom, the stronger C-D bond would favor the more strongly bonded AD liquid state to a greater degree than the weaker C-H bond prefers A-H. Therefore, liquid AD would form more readily than liquid AH at any given instant in time and the  $K_h/K_d$  ratio will be less than one (*i*-KDIE) because  $K_d$  would be larger than  $K_h$ .



Upon achieving complete liquefaction, the HMX decomposition enters the decay period where the autocatalytic rate curve reveals a third linear segment. A 2° KDIE with a  $k_h/k_d$  ratio equal to 1.13 results and provides evidence that covalent ring C-N bond rupture constitutes the rate-controlling step in liquid phase HMX decomposition.<sup>7</sup> Assignment of the rate-controlling ring C-N bond rupture as a true 2° KDIE and not as a masked or diluted 1° KDIE, as in TNT's decay period, is confirmed by comparative HPLC determined HMX concentration and HMX weight loss measurements on liquid N<sub>2</sub> quenched IDSC samples taken at different times along the decomposition curve. The visual absence of any condensed phase decomposed product in the IDSC sample pan at the completion of the decomposition run also supports this 2° KDIE assignment.<sup>7</sup>

The appearance of three different types of KDIE, each during the HMX thermochemical decomposition in dissimilar condensed phases (solid, mixed melt, liquid), shows that HMX does not decompose by a single mechanistic pathway; rather, HMX thermochemical decomposition is a chemical process consisting of at least three different mechanistic pathways, each with its own rate-controlling step that is dependent upon the predominant HMX physical state. The rate-controlling step in solid state decomposition is covalent C-H bond rupture (1° KDIE); the mixed melt phase apparently is controlled by the rate at which the attractive intermolecular crystal lattice forces are weakened by thermal activation (*i*-KDIE), and covalent ring C-N bond rupture is the rate-controlling step (2° KDIE) for the liquid phase. Further verification of the HMX's rate-controlling solid state C-H bond rupture comes from an HMX/HMX- $d_8$  thermochemical decomposition investigation using the isothermal thermal gravimetric analysis (TGA) method<sup>10</sup>. TGA assumes the reaction rate is proportional to a compound's weight loss as a function of time, and is valid for compounds like HMX or RDX where decomposition produces gaseous rather than condensed phase products. Induction period  $I_d/I_h$  ratios determined by TGA over a 235–254°C (508–527 K) temperature range for HMX and HMX- $d_8$  gives

an average KDIE value equal to 1.91 and defines a 1° KDIE. TGA rate constant ratios ( $k_h/k_d$ ) taken between 235–282°C (508–555K) at the 25 percent sample decomposition point also produce an average 1° KDIE (2.07) value.<sup>10</sup>

The two dimensional chemical structure of the eight-membered cyclic HMX/HMX- $d_8$  molecule and its six-membered cousin RDX/RDX- $d_6$  are similar (Figure 11), but their chemical behavior sometimes differs. One

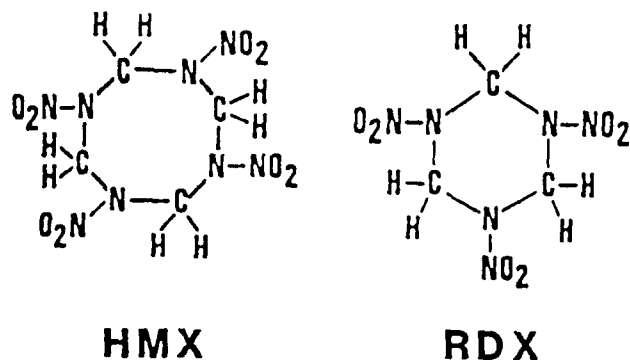


Figure 11. The HMX and RDX chemical structures.

difference is displayed in its thermochemical decomposition. Both TGA<sup>10</sup> and IDSC<sup>35</sup> have been used in mechanistic KDIE investigations of RDX and its RDX- $d_6$  deuterium labeled analogue. Isothermal TGA provides an average 1° KDIE value of 1.54 between 206–216°C (429–489 K) for the liquid phase RDX thermochemical decomposition (mp RDX = 203°C or 476 K), and a 1° KDIE value of 1.51 for apparent solid state RDX decomposition between 199–202°C (392–475 K).<sup>10</sup> This suggests both the RDX solid and liquid thermochemical decomposition processes have covalent C–H bond rupture as the rate-controlling mechanistic step. Mechanistic IDSC investigation of liquid phase RDX and RDX- $d_6$  at 237°C (510K) produces a pseudo first order rate whose  $k_h/k_d$  rate constant ratio gives a 1° KDIE equal to  $1.74 \pm 0.2$  and again confirms that covalent C–H bond rupture is the rate-controlling step for RDX liquid state decomposition.<sup>35</sup> This result from both TGA<sup>10</sup> and IDSC<sup>35</sup> investigations contrasts with the IDSC<sup>7</sup> determined HMX result. While covalent C–H bond rupture seems to be the rate-controlling step in the liquid phase RDX decomposition process,<sup>10, 35</sup> covalent ring C–N ring bond rupture is the rate-controlling step for liquid phase HMX.<sup>7</sup> Both HMX and RDX appear to exhibit the same rate-controlling C–H bond rupture in their solid state thermochemical decomposition process.<sup>7, 10</sup>

### 3. Conclusion

The kinetic deuterium isotope effect (KDIE) selectively identifies the slowest rate-controlling mechanistic step amid the numerous chemical reaction sequences that drive the complex thermochemical decomposition process followed by energetic materials. This kinetically based rate-controlling mechanistic step ultimately determines the rate at which the overall thermochemical



decomposition process and its associated energy release may proceed. Condensed phase KDIE mechanistic investigations of various energetic materials (TNT, HNBB, TATB, HMX, RDX) and their analogous deuterium labeled compounds, (TNT-d<sub>3</sub>, HNBB-d<sub>4</sub>, TATB-d<sub>6</sub>, HMX-d<sub>8</sub>, RDX-d<sub>6</sub>), are easily accomplished using isothermal differential scanning calorimetry (IDSC) and isothermal thermogravimetric analysis (TGA) methods. Condensed phase KDIE investigations conducted by IDSC analysis reveal that covalent chemical bond rupture, or in one case, destruction of attractive intermolecular crystal lattice forces, cause this rate-controlling mechanistic step in the thermochemical decomposition process. The rate-controlling step can show a mechanistic dependence on an energetic compound's physical state and change as the energetic compound moves from one physical state to another. This demonstrates that thermochemical decomposition should not be pictured as having a single mechanistic pathway; rather it is a complex chemical process that may involve several potential mechanistic pathways, each with its own rate-controlling step. Various kinetically determined experimental parameters can be used to identify the KDIE from which one identifies the rate-controlling step in an energetic compound's thermochemical decomposition process. These include rate constants, induction times, critical temperatures, burn rates, and impact sensitivities which are all related directly or indirectly to kinetic reaction rates. The condensed phase KDIE approach can be extended from the milder thermochemical decomposition process into more drastic high energy incidents that all likely involve a rapid pyrolytic decomposition/deflagration of an energetic material. The KDIE determined rate-controlling step, therefore, provides a common experimental feature for comparing mechanistic similarities or differences among various drastic high energy phenomena represented by rapid pyrolytic decomposition/ deflagration, combustion, thermal explosion and detonation. This is addressed in the follow-on paper entitled, "Mechanistic Relationships of the Decomposition Process to Combustion and Explosion Events from Kinetic Deuterium Isotope Effect Investigations".

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# MECHANISTIC RELATIONSHIPS OF THE DECOMPOSITION PROCESS TO COMBUSTION AND EXPLOSION EVENTS FROM KINETIC DEUTERIUM ISOTOPE EFFECT INVESTIGATIONS

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**ABSTRACT.** The condensed phase kinetic deuterium isotope effect (KDIE) approach directly determines the overall rate-controlling mechanistic step of an energetic material's complex thermochemical decomposition process. This second paper discusses extending the KDIE approach into progressively more drastic high temperature/pressure/rate regimes encountered with pyrolytic decomposition/deflagration, combustion, thermal explosion, and detonation incidents in order to determine the rate-controlling step of each. This rate-controlling step provides a common basis for comparing the mechanistic similarities or differences among these high energy incidents; and possible relationships between the thermochemical decomposition process and higher order combustion or explosion incidents are described for HMX, RDX, TATB, and TNT. The KDIE determined rate-controlling step between a pure nitramine compound and a formulated energetic material also is compared.

## 1. Introduction

The condensed phase kinetic deuterium isotope effect (KDIE) approach directly identifies the rate-controlling mechanistic step of an energetic material's thermochemical decomposition process.<sup>1-4</sup> The usefulness of this condensed phase KDIE approach not only applies to thermochemical decomposition studies, it also can be extended into mechanistic investigations of progressively more drastic high energy incidents like rapid pyrolytic decomposition/deflagration<sup>3</sup>, combustion<sup>5</sup>, thermal explosion<sup>2,3</sup> and detonation.<sup>4,6</sup> Extension of the KDIE into these higher pressure/temperature/rate regimes provides the rate-controlling step as a common experimental parameter and permits a direct comparison of mechanistic similarities or differences that promote or generate these high energy incidents.<sup>7</sup> Because the kinetically regulated rate-controlling mechanistic step ultimately determines the overall or global rate at which a high energy incident proceeds, it inherently must be an important consideration for computationally modeling or experimentally tailoring an energetic material's energy releasing behavior.

For this discussion, the five high energy incidents cited are defined in two categories. Thermochemical decomposition and rapid pyrolytic decomposition/deflagration are referred to as energetic processes driven by many complex chemical reactions proceeding in parallel and sequentially. Combustion, thermal explosion, and detonation are referred to as energetic events where an event is composed of at least two different interactive energetic processes. A high energy incident is a collective term for either a chemically driven high energy process or event. The pyrolytic decomposition/deflagration process is defined here as an

|                    |                                      |
|--------------------|--------------------------------------|
| Process. . . . .   | comprised of many chemical reactions |
| Event. . . . .     | comprised of more than one process   |
| Incident . . . . . | either a process or event            |

extremely fast, thermally activated conversion of a condensed phase energetic material into gaseous decomposition products without a visual flame; this contrasts with the slower and milder thermochemical decomposition process found in isothermal differential scanning calorimetry (IDSC) or thermal gravimetric analysis (TGA) studies which proceeds over visually discernable seconds or minutes. Because both processes can convert condensed phase energetic materials like TNT, TATB, RDX, and HMX into the gaseous products needed for promoting or sustaining combustion, thermal explosion, and detonation events, they likely play a role in these three energetic high pressure/temperature events.

The previous paper, "Mechanistic Investigations of Condensed Phase Energetic Material Decomposition Processes Using the Kinetic Deuterium Isotope Effect," discusses applying the condensed phase KDIE approach to the slow ambient pressure thermochemical decomposition process of specific energetic nitroaromatic and nitramine materials. It covers the KDIE concept itself and reviews previous condensed phase KDIE investigations in order to illustrate the various analytical methods and evaluation techniques used to detect the KDIE. The earlier paper further illustrates how the KDIE identifies the kinetically regulated rate-controlling mechanistic step; and with HMX, it demonstrates that thermochemical decomposition is a complex chemical process whose rate-controlling step may change as a compound's physical state is altered. This paper addresses extending the condensed phase KDIE approach beyond the slow ambient pressure thermochemical decomposition process into the progressively more drastic, higher rate/temperature/pressure regimes represented by the pyrolytic decomposition/deflagration process, plus combustion, thermal explosion, and detonation events. Because the condensed phase KDIE approach has been used most extensively in mechanistic investigations with HMX, and because HMX apparently displays a mechanistic dependence on its physical state, KDIE investigations of HMX's high energy incidents will be reviewed first and the rate-controlling step found in each event will be compared. Following the HMX discussion, the energetic compounds RDX, TATB and TNT are also addressed to illustrate the mechanistic relationships which possibly exist between their thermochemical decomposition process and higher order combustion, thermal explosion, and detonation events.

## 2. Discussion

### 2.1 HMX KDIE-DETERMINED MECHANISTIC RELATIONSHIPS

The slow ambient pressure thermochemical decomposition process of HMX may involve more than one mechanistic pathway and specific rate-controlling step. Isothermal DSC (IDSC) investigation of the HMX and deuterium labeled HMX- $d_8$  compounds over a 551–553 K temperature range (mp HMX = 555 K), reveal three dissimilar KDIE values (Figure 1), and each occurs in a different physical state (Figure 2).<sup>3</sup> The early induction period reveals a 1° KDIE which indicates covalent C–H bond rupture of the HMX molecule, or C–H bond

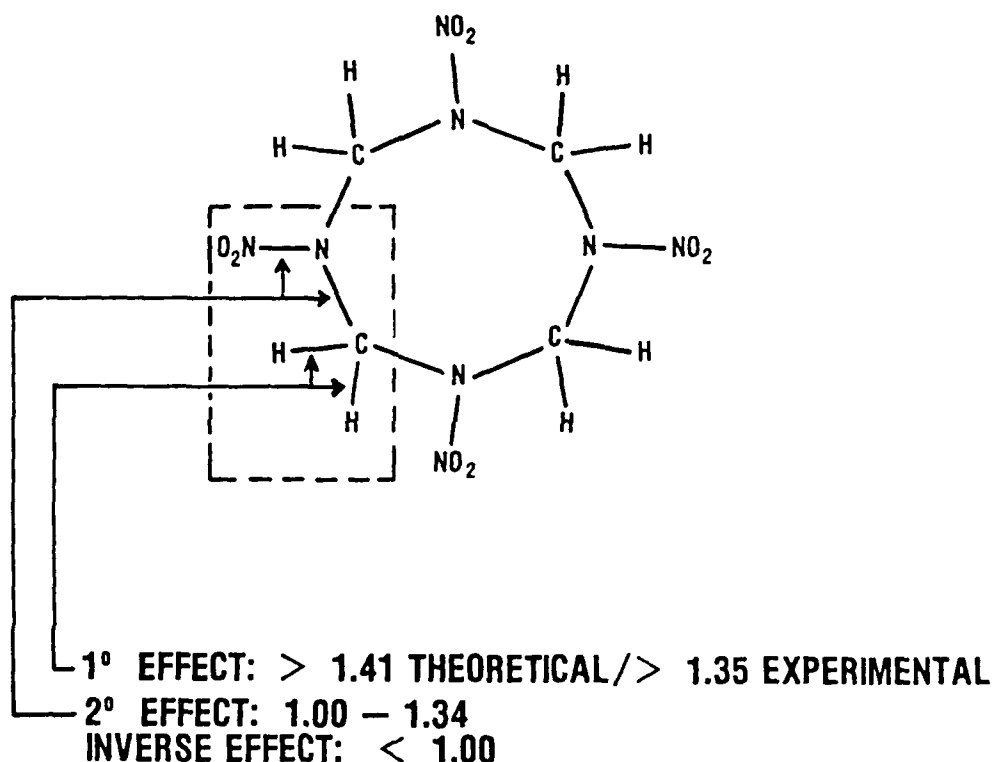


Figure 1. Possible KDIE types in the HMX molecule or structural fragment.<sup>3, 5</sup>

dissociation in an HMX condensed phase derivative, is the rate-controlling mechanistic step in solid state decomposition. Solid state C–H bond rupture as a rate-controlling step is also indicated by HMX and HMX- $d_8$  isothermal TGA analysis.<sup>4</sup> As the IDSC decomposition of HMX enters a short-lived mixed melt phase, an apparent inverse KDIE ( $i$ -KDIE) results possibly caused by the C–H or C–D bond contracting; this suggests that a thermal weakening of the attractive intermolecular crystal lattice forces constitutes the mixed melt phase's rate-controlling step.<sup>3</sup> Upon complete liquification, a 2° KDIE shows ring C–N

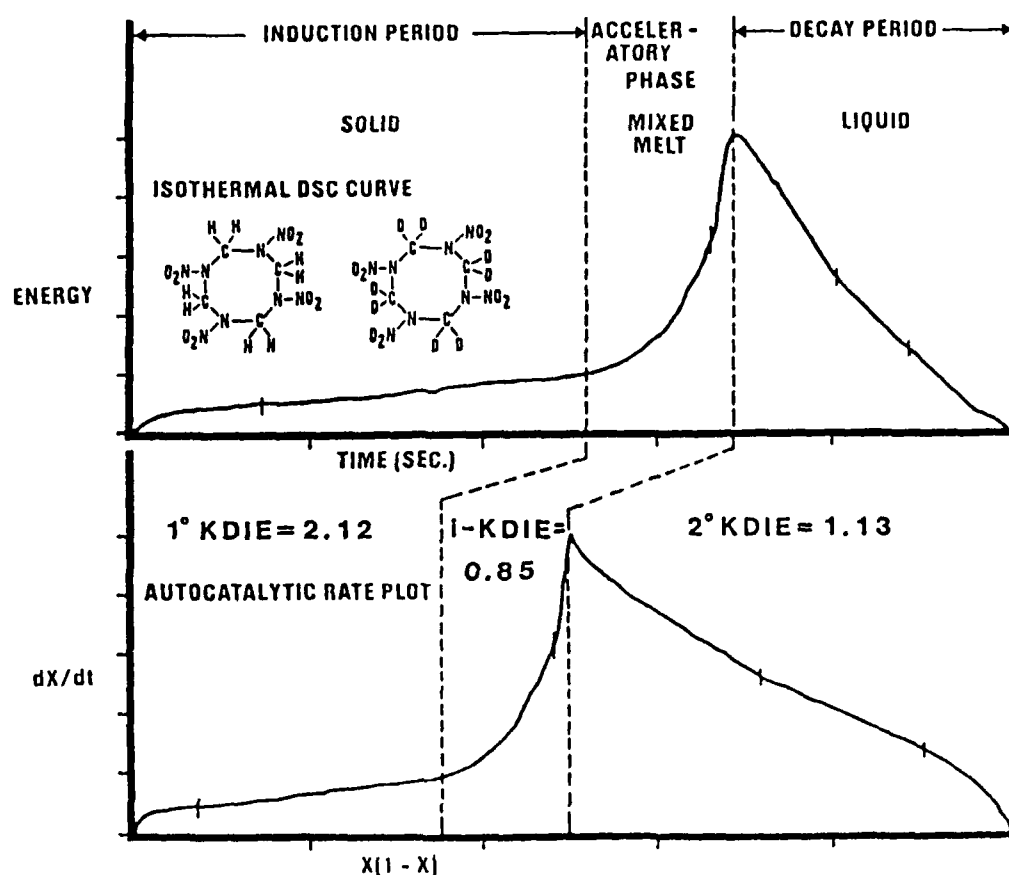


Figure 2. (TOP) Isothermal DSC curve of the HMX thermochemical decomposition process. (BOTTOM) Autocatalytic rate plot of the HMX-thermochemical decomposition curve for HMX and HMX- $d_8$ .<sup>3</sup>

bond rupture or C-N bond rupture in a liquid phase ring fragment, as being the liquid state's rate-controlling step.<sup>3</sup> These results (Table 1) reveal HMX thermochemical decomposition is not a single mechanistic pathway with one rate-controlling step; rather, it is a complex process consisting of at least three different mechanistic pathways. Each mechanistic pathway has its own unique rate-controlling step, and this rate-controlling step is dependent upon the

Table I. HMX Thermochemical Decomposition KDIE Values<sup>3</sup>

| <u>Solid State</u> | <u>Mixed-Melt</u> | <u>Liquid State</u> |
|--------------------|-------------------|---------------------|
| $2.21 \pm 0.2$     | $0.85 \pm 0.2$    | $1.13 \pm 0.1$      |
| 1° KDIE            | 1-KDIE            | 2° KDIE             |



predominant physical state of HMX.<sup>3</sup> The appearance of three different HMX physical states during the IDSC investigation likely results from the boat pan configuration used.<sup>7a,b</sup> The sample pans are covered, but are not sealed and gaseous products generated during the HMX decomposition can gradually escape (Figure 3). During the early portion of the HMX decomposition (Figure 2), the

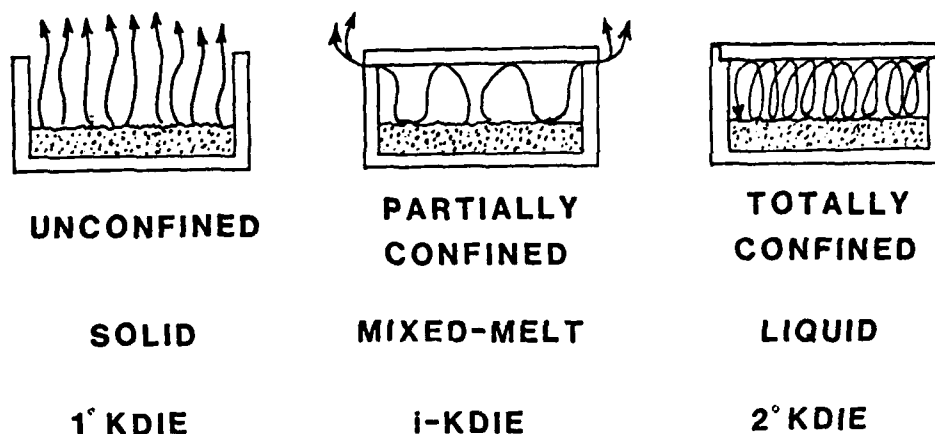


Figure 3. Illustration of possible HMX gaseous and solid state heterogeneous phase interactions during the thermochemical decomposition process.

small amount of gaseous products generated can escape; but as the concentration of gaseous products increase more rapidly with time, not all immediately escape. The gaseous HMX decomposition products build up and begin to act as impurities with the solid HMX sample causing a physical melting point lowering, and bring the HMX sample into the mixed melt phase even though the decomposition is conducted isothermally slightly below the HMX melting point.<sup>3, 5b</sup> As the decomposition progresses, an even higher concentration of gaseous products is generated in the sample pan, and complete HMX liquification results to form the HMX liquid phase during the latter portion of the IDSC curve. Two other condensed phase KDIE experiments involving a pyrolytic decomposition/deflagration process and the thermal explosion event support this mechanistic chemical scenario.<sup>3</sup>

An ambient pressure, isothermal pyrolytic decomposition/deflagration of HMX and HMX- $d_8$  conducted with a high heating rate pyroprobe gun at 21 degrees (534 K) below the HMX melting point (555 K), produces a 1° KDIE with a value slightly over 3.00 (Table II).<sup>3</sup> Lightly pressed HMX or HMX- $d_8$  powder disks are placed into an experimental pyroprobe apparatus where gaseous

Table II. HMX Pyrolytic Decomposition/Deflagration KDIE Values<sup>3</sup>

| Run | Temp (K) | KDIE           | Type |
|-----|----------|----------------|------|
| A   | 534      | $3.02 \pm 0.6$ | 1°   |
| B   | 534      | $3.06 \pm 0.5$ | 1°   |

decomposition products are rapidly carried away so that gaseous decomposition products do not build up, or interact with the solid HMX sample and cause a physical melting point lowering (Figure 4). The solid HMX and HMX-d<sub>8</sub> samples instantaneously convert to gaseous products with no visible flame (Figure 5). By induction time comparison,<sup>1</sup> a 1<sup>0</sup> KDIE ( $t_{id}/t_{ih} > 3.00$ ) shows that solid state covalent C-H bond rupture is the mechanistic rate-controlling step for this rapid pyrolytic decomposition/deflagration,<sup>3</sup> just as it is in the slow thermochemical decomposition process studied by IDSC<sup>3</sup> and TGA.<sup>4</sup>

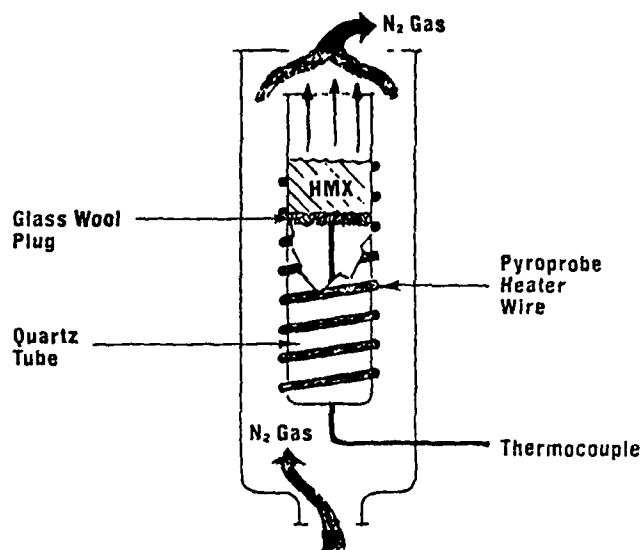


Figure 4. Rapid high heating rate pyroprobe apparatus and assembly for HMX and HMX-d<sub>8</sub>.<sup>3</sup>

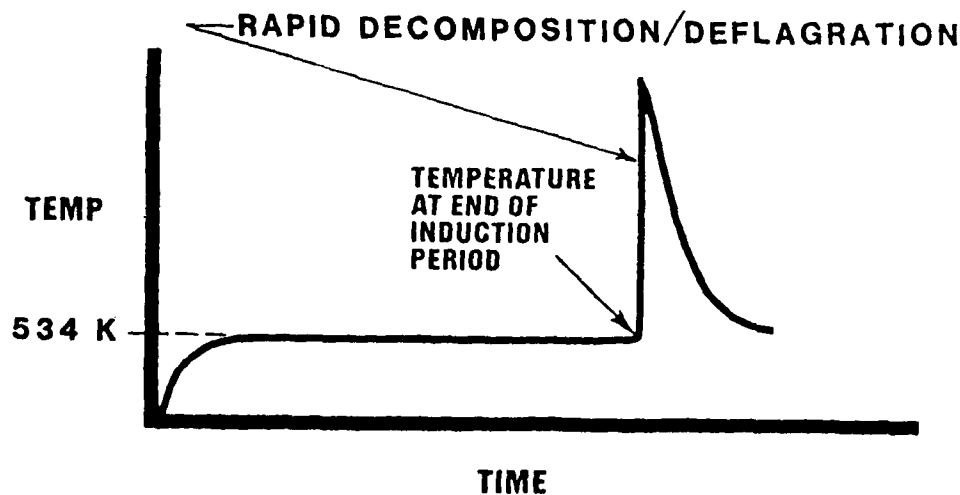


Figure 5. Isothermal rapid pyrolytic decomposition/deflagration curve of HMX and HMX-d<sub>8</sub>.<sup>3</sup>

The thermal explosion event produced during HMX and HMX-d<sub>8</sub> time-to-explosion experiments reveals an *i*-KDIE. This *i*-KDIE suggests the rate-controlling mechanistic step results from the rate at which the attractive HMX intermolecular crystal lattice forces are weakened by thermal activation.<sup>3</sup> Isothermal time-to-explosion experiments with a normal and deuterium labeled compound show a correlation between the two energetic compounds' critical temperature difference and the type of KDIE the same compounds display in an IDSC thermochemical decomposition experiment.<sup>2</sup> Critical temperature ( $t_c$ ) represents the lowest constant surface temperature at which a given energetic material of a specific size and shape will self-heat catastrophically to a thermal explosion event in a modified Henkin Test apparatus.<sup>2, 3, 8</sup> The first KDIE study relating mechanism with energetic material sensitivity<sup>2</sup> discloses that energetic compounds producing a higher critical temperature with their deuterium labeled analogue ( $t_{cd}$ ), correlate with a positive ( $1^0$  or  $2^0$ ) KDIE determined during an IDSC analyzed thermochemical decomposition process. Normal or unlabeled compounds that have a critical temperature ( $T_{ch}$ ) equal to or greater than its deuterium labeled analogue, apparently correlate with an *i*-KDIE observed in the complementary IDSC investigation (Table III).<sup>2</sup> This relationship apriori seems

Table III. Thermal Explosion and Thermochemical Decomposition KDIE Comparison

| Thermal Explosion Event | Thermochemical Decomp. Process (IDSC) |
|-------------------------|---------------------------------------|
| $T_{cd}/T_{ch} > 1.00$  | $1^0$ or $2^0$ KDIE                   |
| $T_{cd}/T_{ch} < 1.00$  | inverse KDIE                          |

justified since a higher  $T_c$  would indicate the kinetically regulated chemical reactions promoting or generating the thermal explosion event occur more slowly (smaller overall rate constant,  $k$ ) at a lower temperature; and thus,  $k_h/k_d \propto T_{cd}/T_{ch} \propto t_{id}/t_{ih}$ . HMX affords a critical temperature (257°C) that is 15 degrees above HMX-d<sub>8</sub> (242°C) as illustrated by Figure 6.<sup>3</sup> This correlates to the *i*-KDIE found during the mixed-melt phase in the IDSC thermochemical decomposition investigation, and suggests the thermal explosion event occurs with HMX predominantly in the mixed melt phase.<sup>3</sup> Because the HMX or HMX-d<sub>8</sub> sample is totally confined during the time to explosion test, a rapid high pressure build-up occurs, and the gaseous decomposition products cannot escape. Instead, these gaseous impurities interact with the solid HMX sample and apparently produce a rapid melting point lowering to quickly bring the HMX into the mixed-melt phase where the thermal explosion event occurs before liquefaction is completed. Heterogenous gas-condensed phase interactive reactions have been observed to increase with higher pressure<sup>9</sup> and take on a greater importance in a nitramine's rapid thermoanalysis.<sup>10</sup> As revealed by the *i*-KDIE and possible C-H/C-D bond contraction, the rate-controlling mechanistic step in a highly confined HMX thermal explosion event depends upon the rate at which the HMX intermolecular molecular crystal lattice forces are overcome by thermal activation. In contrast, the unconfined, ambient pressure HMX pyrolytic decomposition/deflagration process where appreciable solid state HMX/gaseous product interactions are avoided, shows solid state C-H bond rupture as the rate-controlling mechanistic step (Figure 3).

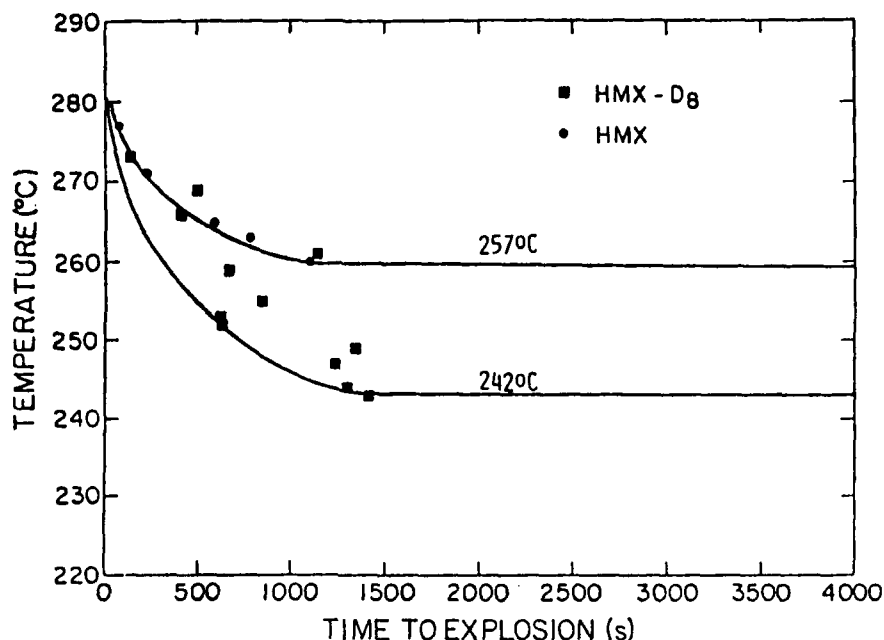


Figure 6. Critical temperature of HMX and HMX-d<sub>8</sub> determined from isothermal time-to-explosion tests.<sup>3</sup>

Sample confinement apparently represents one external boundary condition that directly influences the predominant HMX physical state present during a given energetic process or event; this in turn, dictates the rate-controlling mechanistic step. It appears there is a mechanistic correlation with the KDIE-determined rate-controlling steps observed in the ambient pressure, slow thermochemical decomposition process with both the rapid pyrolytic decomposition/deflagration process and the thermal explosion event. This causes one to wonder if a correlation exists between the high pressure combustion event and the ambient pressure thermochemical decomposition process.

Combustion represents an intermediate pressure/temperature/rate regime between the rapid pyrolytic decomposition/deflagration process and thermal explosion event. When the condensed phase KDIE approach is applied to the static high pressure combustion of pressed HMX and HMX-d<sub>8</sub> solid pellet samples, a significant KDIE results and verifies a substantial degree of chemical kinetic control for this event.<sup>5</sup> The combustion event undoubtedly is a very complex phenomenon involving both interactive chemical and physical processes proceeding among various condensed and gaseous physical states. All three HMX condensed phase physical states (solid, mixed-melt, liquid) could be present during combustion, and the far more extensively investigated gaseous flame consists of several flame stages and reaction zones.<sup>11-14</sup> Some conceptual simplification is necessary to address the relevant mechanistic points revealed by the KDIE combustion study of HMX. The combustion event may be viewed as consisting of two interacting processes: (1) a condensed phase rapid decomposition/deflagration process that produces the gaseous decomposition products needed to feed and sustain the second process; (2) a gas phase flame oxidation process that converts these gaseous decomposition products to the final combustion products<sup>5, 7</sup> (Figure 7). Each complex process considered separately

has many chemical reactions, and each has its own rate-controlling mechanistic step; but, of the two, one rate-controlling step will occur more slowly than the other. This slower rate-controlling mechanistic step ultimately determines the overall or global HMX burn rate.<sup>5, 7</sup>

The combustion KDIE is determined from the burn rate ratios ( $r_{bh}/r_{bd}$ ) of the cylindrical HMX and HMX-d<sub>8</sub> pellets made from identically synthesized<sup>3, 5, 15, 16</sup> HMX and HMX-d<sub>8</sub> powders. The HMX and HMX-d<sub>8</sub> pellet samples are pressed to 96–97 percent of the HMX single crystal density assuring any burn rate

## 1. LIQUID/SOLID PHASE

## 2. GAS PHASE

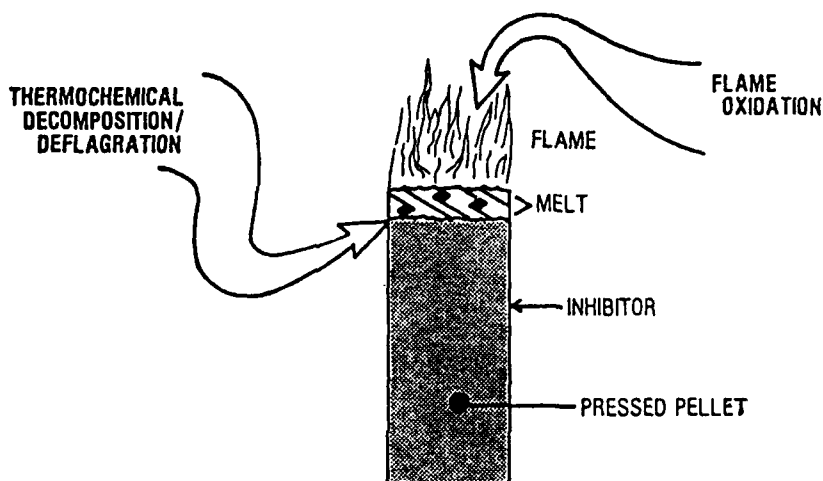


Figure 7. Representation of the HMX and HMX-d<sub>8</sub> pressed pellet combustion event.<sup>5</sup>

differences that cause a KDIE result solely from the deuterium isotope substitution and not from sample history, purity, particle size or void distribution. This is a necessary condition for KDIE validity. High pressure window bomb combustion produces a significant KDIE over a 500 psig (3.55 MPa) to 1500 psig (10.4 MPa) pressure range (Table IV). A 1<sup>0</sup> KDIE results at 500 psig (3.55 MPa) and 1000 psig (6.99 MPa) pressures indicating C–H bond rupture is this event's rate-controlling step. The KDIE value at 1500 psig (10.4 MPa) at first glance, appears low for a 1<sup>0</sup> KDIE; but, it is within the experimentally accepted minimum 1<sup>0</sup> KDIE value of 1.35<sup>18-20</sup> at a statistical 95% confidence level range. The possibility the KDIE at 1500 psig (10.4 MPa) represents a very large 2<sup>0</sup> KDIE involving a sudden mechanistic change from a rate-controlling C–H bond rupture to a ring C–N bond rupture also should be considered;<sup>5a</sup> but, when the experimental KDIE values are mathematically extrapolated to standard temperature, a 1<sup>0</sup> KDIE still remains plausible. When one considers the maximum 2<sup>0</sup> KDIE value at standard temperature theoretically would be 1.74 squared or 3.03<sup>21</sup> and that a true 2<sup>0</sup> KDIE value of only 1.13 is seen in the 551–553 K temperature range for the HMX thermochemical decomposition process<sup>3</sup> which calculates to 1.32 at standard temperature<sup>5a, 7a</sup>, a

Table IV. HMX and HMX-d<sub>8</sub> Burn Rates (in/s) and KDIE (r<sub>bh</sub>/r<sub>bd</sub>) Values.<sup>5</sup>

| 500 psig (3.55 MPa)                      |                                       | 1000 psig (6.99 MPa)       |                    | 1500 psig (10.4 MPa) |                    |
|--|---------------------------------------|----------------------------|--------------------|----------------------|--------------------|
| HMX(r <sub>bh</sub> )                    | HMX-d <sub>8</sub> (r <sub>bd</sub> ) | HMX                        | HMX-d <sub>8</sub> | HMX                  | HMX-d <sub>8</sub> |
| 0.257                                    | 0.167                                 | 0.464                      | 0.306              | 0.716                | 0.604              |
| 0.253                                    | 0.219                                 | 0.505                      | 0.311              | 0.690                | 0.596              |
| 0.284                                    | 0.183                                 | 0.529                      | 0.320              | 0.698                | 0.502              |
| —  | 0.192                                 | —                          | 0.308              | —                    | —                  |
| <u>Ave. r<sub>b</sub>:</u>               |                                       |                            |                    |                      |                    |
| 0.265±.02                                | 0.193±.03                             | 0.499±.03                  | 0.331±.01          | 0.701±.01            | 0.576±.06          |
| <u>Expl. KDIE* (553 K)<sup>17</sup>:</u> |                                       |                            |                    |                      |                    |
| 1.37±0.2 (1 <sup>0</sup> )               |                                       | 1.60±0.2 (1 <sup>0</sup> ) |                    | 1.24±0.2 (?)         |                    |
| <u>Std. KDIE (298K)<sup>18</sup>:</u>    |                                       |                            |                    |                      |                    |
| 3.26                                     |                                       | 3.80                       |                    | 2.95                 |                    |

\*Error limits for KDIE values are shown at the 95% confidence level

masked 1<sup>0</sup> KDIE remains a possibility. The KDIE generally shows a temperature dependence and decreases with increasing temperature; so, KDIE values semi-quantitatively can be extrapolated mathematically to standard temperature using appropriate equations.<sup>18</sup> It should also be pointed out, true 1<sup>0</sup> KDIE values can be diluted or masked to appear as a 2<sup>0</sup> KDIE because of other interfering reaction pathways which have their own rate-controlling mechanistic step. In such a case, the true 1<sup>0</sup> KDIE would appear as a larger number if its specific reaction pathway were the only one occurring or were the only one being detected. An example of masking appears in the IDSC thermochemical decomposition of TNT and TNT-d<sub>3</sub>.<sup>1</sup> This possible masking of the KDIE value at 1500 psig (10.4 MPa) is discussed in greater detail elsewhere;<sup>5</sup> but, the appearance of significant KDIE values from over the 500 psig (3.55 MPa) to 1500 psig (10.4 MPa) pressure range verifies a substantial degree of kinetic control for the combustion event.<sup>5</sup> The 1<sup>0</sup> KDIE values at 500 psig (3.55 MPa) and 1000 psig (6.99 MPa) reveal covalent C-H bond rupture as being the rate-controlling mechanistic step for the global or overall HMX burn rate in this pressure range. It further suggests this kinetically regulated rate-controlling C-H bond rupture may occur in the portion of the combustion event that involves the solid state rapid decomposition/deflagration process (Figure 7).<sup>5</sup> While the gas phase flame oxidation process has its own rate-controlling mechanistic step, past studies with the HMX and RDX decomposition process within a similar temperature range, show a decomposition rate increase as one proceeds from the solid to liquid to gaseous state.<sup>22</sup> This suggests the observed kinetic rate-controlling C-H bond rupture step could occur most slowly in the condensed phase's decomposition/deflagration process; and since the 1<sup>0</sup> KDIE has been observed for HMX only in the solid state<sup>3</sup>, it follows that covalent solid state C-H bond dissociation ultimately may exercise a substantial kinetic control over the global HMX burn rate. Control of the HMX burn rate by condensed phase reactions recently has also been postulated from other experimental findings<sup>10, 13, 23-24</sup> and micro-thermocouple studies reveal a solid phase temperature gradient profile that is

high enough to produce a rapid HMX decomposition/deflagration in either HMX<sup>13</sup> or in an HMX based propellant.<sup>24</sup> The appearance of a significant KDIE in the HMX combustion event and its implication of a kinetically based rate-controlling solid state C-H bond rupture, strongly indicate that mechanistic condensed phase combustion characteristics can no longer be ignored as they have been in the past. While previous theoretical and experimental mechanistic studies of the gas phase chemical process abound, only by understanding the mechanistic features of both the condensed phase decomposition/deflagration process, and gas phase flame oxidation process, plus their interaction with one another, will adequate computational codes be developed which accurately describe and predict the combustion behavioral characteristics of a specific energetic material.

The mechanistic importance of kinetically controlled condensed phase reaction contributions in determining the overall or global burn rate of a pure energetic compound is further illustrated by the KDIE investigation of laboratory scale HMX and HMX-d<sub>8</sub> based propellant formulations. Parallel window bomb combustion experiments conducted at 1000 psig (6.99 MPa) with pure HMX and HMX-d<sub>8</sub> samples, as well as an HMX/CW5<sup>25</sup> propellant and its HMX-d<sub>8</sub>/CW5 analogue, give essentially the same KDIE value (Table V).<sup>26</sup> These samples are prepared in a No. 3 gelatin capsules (Eli Lilly Co) at a density of 1.62 g/cm<sup>3</sup>. The appearance of the same probable 1<sup>0</sup> KDIE value for the pure HMX and HMX/CW5 propellant samples strongly suggests the same solid state covalent C-H bond rupture found in pure HMX is also the rate-controlling mechanistic step which kinetically regulates the formulated, urethane cured propellant burn rate.<sup>7a, 26</sup>

Table V. HMX and HMX/CW5 Propellant KDIE Values at 1000 psig (6.99 MPa).<sup>26</sup>

|  | <u>HMX/HMX-d<sub>8</sub></u> | <u>HMX/CW5&amp;HMX-d<sub>8</sub>/CW5</u> |
|--|------------------------------|--|
| Expl KDIE (553 K) <sup>17</sup>                            | 1.30 ± .05                   | 1.29 ± .09                               |
| Std KDIE (298 K) <sup>18</sup>                             | 3.09                         | 3.07                                     |
| Max Theo. 2 <sup>0</sup> KDIE (298 K) = 3.03 <sup>21</sup> |                              |  |

While the KDIE values in Table V fall slightly below the experimental 1.35 value for a pure compounds minimum high temperature value, and are somewhat lower than those in the pressed pellet combustion study of the pure pressed pellet HMX samples (Table IV), the KDIE possibly is masked by interfering reactions from combustion of the gelatin capsules which could have a different rate-controlling mechanistic step from the HMX or HMX/CW5 propellant formulation itself. Still, the 95% confidence level statistical variation places these presumed 1<sup>0</sup> KDIE values within the same confidence level range as the earlier HMX pressed pellet KDIE combustion results. When mathematically normalized to standard temperature using a 1<sup>0</sup> KDIE equation,<sup>18</sup> the standard temperature KDIE values in Table V also slightly exceed the maximum theoretical 2<sup>0</sup> KDIE value of HMX at 298 K and are, therefore, considered plausible representations of a 1<sup>0</sup> KDIE. This 1<sup>0</sup> KDIE assignment is further supported by the fact that the only

confirmed 2° KDIE seen around 552 K for an energetic compound, is 1.13 for HMX during its liquid phase thermochemical decomposition<sup>3</sup> and equates only to a 1.32 2° KDIE value<sup>18</sup> at standard temperature (298 K).<sup>7a</sup>

The first mechanistic KDIE correlation of the thermal decomposition process with explosive sensitivity was accomplished with the thermally initiated nonsteady-state thermal explosion event.<sup>2</sup> The HMX thermal explosion event has been discussed<sup>3</sup> and represents an intermediate temperature/pressure regime between the less drastic combustion event and the high order steady-state detonation event. Mechanistic KDIE detonation investigations recently have been conducted and provide the first correlation between the thermochemical decomposition process and shock-induced detonation using an exploding foil driven flyer plate test.<sup>4, 6</sup>

The shock-induced KDIE detonation of HMX and HMX-d<sub>8</sub> detects a KDIE as the difference between flyer plate velocity (V) needed to shock initiate normal HMX (V<sub>h</sub>) and its deuterium labeled HMX-d<sub>8</sub> analogue (V<sub>d</sub>). The HMX-d<sub>8</sub> demonstrates a small but definitive positive KDIE (V<sub>d</sub>/V<sub>h</sub> > 1.00) where the rate-controlling mechanistic step of HMX-d<sub>8</sub> proceeds more slowly (lower k<sub>d</sub>) than that of HMX (higher k<sub>h</sub>). Thus, k<sub>h</sub>/k<sub>d</sub> has a proportional correlation to V<sub>d</sub>/V<sub>h</sub> because a larger flyer plate velocity (V<sub>d</sub>) is needed to bring the overall slower k<sub>d</sub> value to the same value as k<sub>h</sub> (Table VII), and k<sub>h</sub>/k<sub>d</sub> ∝ t<sub>id</sub>/t<sub>ih</sub><sup>1, 3</sup> ∝ t<sub>cd</sub>/t<sub>ch</sub><sup>2, 3</sup> ∝ r<sub>bh</sub>/r<sub>bd</sub><sup>5</sup> ∝ V<sub>d</sub>/V<sub>h</sub><sup>4, 6</sup>.

Table VII. Exploding Foil Shock Detonation KDIE Values.<sup>4</sup>

| Sample             | Flyer Plate Vel.(mm/μs) | Std Dev | KDIE Type      |
|--------------------|-------------------------|---------|----------------|
| HMX                | 2.37                    | .028    | Positive - ie. |
| HMX-d <sub>8</sub> | 2.27                    | .046    | (1° or 2°)     |

The indirect nature of this KDIE does not permit a quantitative differentiation between a solid state C-H bond rupture (1° KDIE) or liquid state ring C-N bond rupture (2° KDIE) as the rate-controlling mechanistic step, assuming δ-HMX and β-HMX will display the same mechanistic pathways in their thermochemical decomposition process. Certainly, an i-KDIE like that apparently produced in the thermally initiated HMX thermal explosion event<sup>3</sup> does not occur. Recent high pressure diamond anvil cell/FTIR decomposition experiments have been conducted with β-HMX in the GPa pressure range to simulate the pressures closer to that experienced by the detonation event. This study reveals β-HMX decomposition at GPa pressures occurs solely in the solid state.<sup>27</sup> This finding might favor the solid state process as housing the detonation event's rate-controlling mechanistic step where the exploding flyer plate's shock produces an adiabatic compression, which in turn, initiates a rapid pyrolytic solid state β-HMX decomposition/deflagration process that generates or promotes the detonation event before liquefaction can occur.<sup>7a</sup> Interestingly, the high pressure GPa HMX decomposition process provides a linear autocatalytic kinetic plot;<sup>27</sup> this is the same kinetically based autocatalytic behavior found with the ambient pressure IDSC thermochemical decomposition process where a 1° KDIE reveals covalent solid state C-H bond rupture as being the rate-controlling mechanistic step for δ-HMX.<sup>3</sup> For a totally adequate rate-controlling step correlation to be shown between the ambient pressure thermochemical decomposition process's solid state C-H bond dissociation (δ-HMX) and the shock induced detonation



event (likely  $\beta$ -HMX), a high pressure KDIE investigation of  $\beta$ -HMX and  $\beta$ -HMX- $d_8$  is needed.

In all HMX high energy incidents, significant kinetic control is observed using the condensed phase KDIE approach. Most notably, the same physical state dependent rate-controlling mechanistic steps found in the mildest HMX high energy incident, the ambient pressure thermochemical decomposition process, also are mirrored in the more drastic high energy incidents (Table VIII). This

Table VIII. Summary of HMX High Energy Incident Rate-Controlling Steps<sup>7a</sup>

|                                   | 1 <sup>0</sup> KDIE<br>(solid state)<br>(C-H bond) | i-KDIE<br>(mixed melt)<br>(cryst forces) | 2 <sup>0</sup> KDIE<br>(liquid state)<br>(C-N bond) |
|-----------------------------------|--|--|---|
| Thermochemical Decomp             | X  | X  | X   |
| Pyrolytic Decomp/<br>Deflagration | X  |  |   |
| Combustion                        | X  |  |   |
| Thermal Explosion                 |  | X  |   |
| Detonation                        | (X)  | or                                       | (X)   |

suggests that with careful consideration, mechanistic results obtained from slow ambient pressure, thermochemical decomposition KDIE investigations can be extrapolated and used as a preliminary guide for planning future mechanistic studies in the higher order combustion, thermal explosion, and possibly detonation events.<sup>7a</sup> In support of this statement are other extensions of the condensed phase KDIE approach from the ambient pressure thermochemical decomposition process into these more drastic energetic events using energetic compounds other than HMX.

## 2.2 RDX KDIE-DETERMINED MECHANISTIC RELATIONSHIPS

The slow thermochemical decomposition process of both liquid and solid state RDX produces a 1<sup>0</sup> KDIE indicating that C-H bond rupture is its rate-controlling mechanistic step (Figure 8).<sup>4, 28</sup> The same rate-controlling

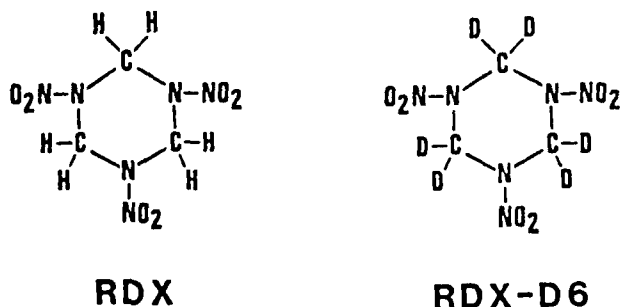


Figure 8. Chemical structure of RDX and RDX- $d_6$ .

C-H bond rupture is also present in the RDX static combustion event at 500 psig (3.55 MPa) and 1000 psig (6.99 MPa).<sup>28</sup> Identically synthesized cylindrical pressed RDX and RDX-d<sub>6</sub> pellets were burned in a window bomb and provide a 1<sup>0</sup> KDIE when their burn rates ratios are calculated (Table IX). For the same reasons that solid state C-H bond rupture might be the rate-controlling step in the HMX combustion event, the rate-controlling C-H bond rupture in RDX

Table IX. RDX Burn Rates (in/s) and Combustion KDIE ( $r_{bh}/r_{bd}$ ) Values<sup>28</sup>

|            | 500 psig (3.55 MPa) |                                 | 1000 psig (6.99 MPa) |                    |
|------------|---------------------|---------------------------------|----------------------|--------------------|
|            | RDX( $r_{bh}$ )     | RDX-d <sub>6</sub> ( $r_{bd}$ ) | RDX                  | RDX-d <sub>6</sub> |
| Ave $r_b$  | 0.297 ± 030         | 0.217 ± 012                     | 0.567 ± .069         | 0.387 ± .032       |
| Expl KDIE* | 1.37 ± 0.2          |                                 | 1.46 ± 0.2           |                    |

\*Error limits for KDIE values are shown at the 95% confidence level

combustion could also come from the solid or liquid state during the pyrolytic decomposition/deflagration process. While there is less data to support RDX condensed phase C-H bond rupture as housing the rate-controlling step that determines its burn rate, both isothermal TGA and IDSC analyses show RDX can undergo significant decomposition even below its melting point.<sup>4, 29</sup> A KDIE mechanistic combustion study of the RDX/CW5 and RDX-d<sub>6</sub>/CW5 propellant<sup>25</sup> reveals C-H bond rupture to be the rate-controlling step for the urethane cured propellant formulation as well as for the pure RDX energetic compound (Table X).<sup>26</sup> The samples are prepared in the same No. 3 gelatin capsules used for the analogous HMX/CW5 propellant KDIE combustion experiment; the density of the pure RDX and RDX/CW5 samples is 1.48 g/cm.<sup>3</sup> Again it appears the pure

Table X. RDX and RDX Propellant KDIE Values at 1000 psig (6.99 MPa).<sup>26</sup>

|   | Pure RDX/RDX-d <sub>6</sub> | RDX/CW5 & RDX-d <sub>6</sub> /CW5 |
|---|-----------------------------|-----------------------------------|
| Expl KDIE (673 K) <sup>30</sup>                           | 1.31 ± .04                  | 1.24 ± .05                        |
| Std KDIE (298 K) <sup>18</sup>                            | 3.73                        | 3.53                              |
| Max Theo 2 <sup>o</sup> KDIE (298 K) = 3.03 <sup>21</sup> |                             |                                   |

nitramine component's rate-controlling mechanistic step is also that which determines a formulated propellant's burn rate.

Impact initiation experiments conducted with a 10 kg weight on RDX just below its ignition threshold and subsequently analyzed by x-ray photoelectron spectroscopy (XPS), suggest both nitroso and triazine type products form within the hot spots created by mechanical impact.<sup>31</sup> The very rapid pyrolytic decomposition/deflagration that causes the hot spots in the RDX sample, converts the RDX to the nitroso and triazine type products on the hot spot surface. The thermally initiated hot spots caused by physical impact could be a prelude to either a thermal explosion,<sup>32</sup> or if shocked stringently enough with an exploding foil plate,<sup>4</sup> a detonation event. It appears the nitroso compounds may form first enroute to the triazine type products.<sup>31</sup> Formation of triazine type products requires a C-H bond rupture to generate the ring C=N double bond

structure for this type of chemical compound and would be consistent with C-H bond rupture as the rate-controlling step. Consistent also with the RDX rate-controlling C-H bond rupture step is a shock-induced KDIE detonation experiment with RDX and RDX-d<sub>6</sub>. Already described for the HMX/HMX-d<sub>8</sub> system, the RDX-d<sub>6</sub> demonstrates a small but definitive positive KDIE ( $V_d/V_h > 1.00$ ) as shown in Table XI.<sup>4</sup> The appearance of a positive KDIE could be consistent with C-H bond rupture as the rate-controlling HMX/HMX-d<sub>8</sub>

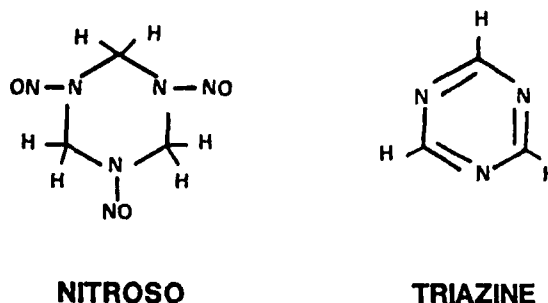


Figure 9. Chemical structure of nitroso and triazine type compounds.

Table XI. Exploding Foil Shock Detonation KDIE Values.<sup>4</sup>

| Sample             | Flyer Plate Vel.(mm/ $\mu$ s) | Std Dev | KDIE Type                           |
|--------------------|-------------------------------|---------|-------------------------------------|
| RDX                | 2.323                         | 0.061   | Positive - ie                       |
| RDX-d <sub>6</sub> | 2.402                         | 0.028   | (1 <sup>0</sup> or 2 <sup>0</sup> ) |

system, the RDX-d<sub>6</sub> demonstrates a small but definitive positive KDIE ( $V_d/V_h > 1.00$ ) as shown in Table XI.<sup>4</sup> The appearance of a positive KDIE could be consistent with C-H bond rupture as the rate-controlling mechanistic step that significantly promotes or generates the detonation event. It appears that the same rate-controlling mechanistic step found in KDIE investigations of the RDX thermochemical decomposition process,<sup>4, 28</sup> may be present in the higher order combustion event<sup>26</sup> and possibly in the process that initiates or promotes the impact induced<sup>31</sup> thermal explosion and shock initiated<sup>4</sup> detonation events.

### 2.3 TATB KDIE-DETERMINED MECHANISTIC RELATIONSHIPS

The slow thermochemical decomposition process of solid TATB produces a 1<sup>0</sup> KDIE indicating amino group N-H bond rupture is its rate-controlling mechanistic step (Figure 10).<sup>2</sup> This decomposition is a complex autocatalytic process involving two sequential reaction pathways. The 1<sup>0</sup> KDIE and rate-controlling N-H bond rupture appear in the first reaction pathway early in the process; and, nmr proton analysis of the condensed phase products found in the second reaction pathway show little or no hydrogen atoms present.<sup>2</sup> The same rate-controlling mechanistic step may be present in TATB's thermal explosion event since TATB-d<sub>6</sub> displays a 12 degree higher critical temperature than its normal hydrogen substituted analogue.<sup>2</sup> This higher TATB-d<sub>6</sub> critical temperature correlates to a positive KDIE (1<sup>0</sup> or 2<sup>0</sup>) with isothermal DSC

analysis. If one assumes the accepted kinetic generality that a reaction rate doubles for each 10 degree temperature rise and that it applies to the kinetically regulated reactions promoting or generating TATB's thermal explosion event, its rate-controlling step would be displaying a  $1^0$  KDIE approximately equal to a 2.4 value.

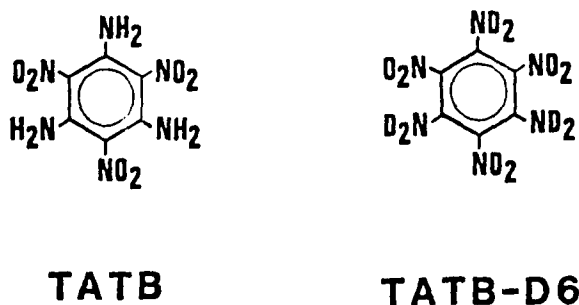


Figure 10. Chemical structure of TATB and TATB-d<sub>6</sub>.

Thermally decomposed TATB condensed phase products have been isolated by repeated thin layer chromatography (TLC) elution, and chemical ionization mass spectrometry (CIMS) analysis reveals at least three furoxan products formed by the loss of H<sub>2</sub> and cyclization of adjacent amino and nitro groups (Figure 11).<sup>33</sup> This must involve N-H bond rupture and is consistent with it being the same

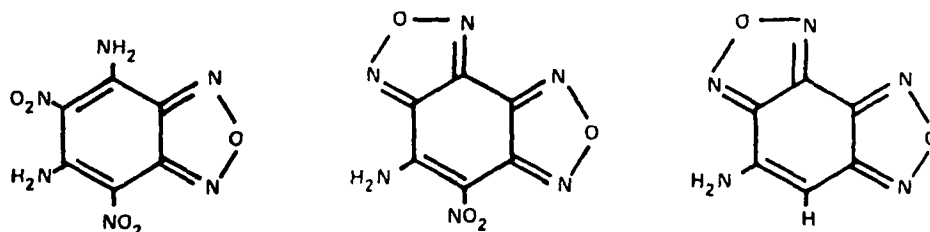


Figure 11. Isolated furazan products from the TATB thermochemical decomposition process.<sup>33</sup>

rate-controlling mechanistic step found in the IDSC decomposition experiment.<sup>2</sup> Impact initiation experiments conduct just below the ignition point of TATB and subsequent XPS, plus CIMS analysis of the rapidly decomposed surface products in the hot spots, show both furoxan 4 and furazan 5 derivatives form from the loss of H<sub>2</sub> and H<sub>2</sub>O respectively (Figure 12).<sup>34</sup> Again, these products are consistent with N-H bond rupture as being the same rate-controlling mechanistic step found by the IDSC analysis of the TATB's slow ambient temperature decomposition process,<sup>2</sup> and likely could be the same rate-

controlling step for both the TATB thermally induced thermal explosion event,<sup>2</sup> and impact initiated<sup>34</sup> thermal explosion event.

## 2.4 TNT KDIE—DETERMINED MECHANISTIC RELATIONSHIPS

The slow thermochemical decomposition process of liquid TNT produces a 1<sup>0</sup>

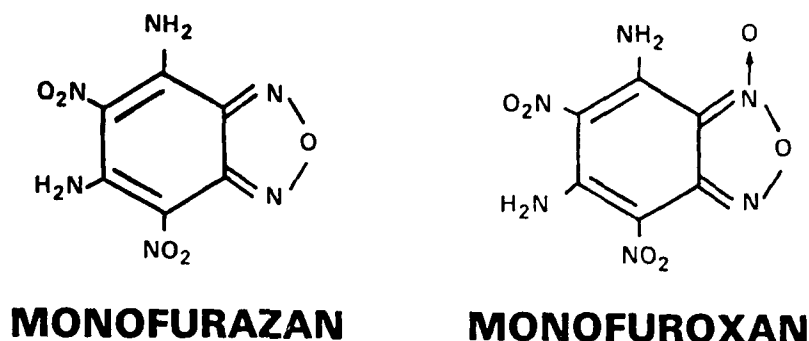


Figure 12. Furazan and furoxan products formed from sub-ignition of TATB by mechanical impact.<sup>34</sup>

KDIE very early in the IDSC analysis decomposition curve and indicates methyl group C—H bond rupture is the rate-controlling mechanistic step (Figure 13).<sup>1</sup> A catalytic product forms in trace amounts by this rate-controlling C—H bond dissociation from the TNT itself and initiates the exothermic portion of the TNT thermochemical decomposition process. Product isolation studies<sup>35,36</sup> and electron paramagnetic resonance (epr) analysis<sup>37,38</sup> identify a number of condensed phase products and a stable nitroxyl radical, formed via methyl group C—H bond rupture during TNT's slow thermochemical decomposition process (Figure 13); an apparent 1<sup>0</sup> KDIE also has been detected in a TNT and TNT-d<sub>3</sub> epr study by comparing the rate of nitroxyl radical formation.<sup>39</sup> Further evidence possibly supporting this C—H bond dissociation as the possible rate-controlling step leading to thermal explosion by impact, or a detonation by shock initiation, also has emerged. Impact initiation experiments conducted just below the ignition point of TNT with a 10 kg weight, and subsequent XPS analyses of SEM identified microscopic hot spot sites, reveal melting occurs at these sites and that three condensed phase products are present.<sup>31,40</sup> These three products (Figure 14) correspond to 4,6-dinitroanthranil, 2,4,6-trinitrobenzaldehydoxime, and 2,4,6-trinitrobenzyl nitrile derived from TNT with the benzyl nitrile possibly formed by loss of H<sub>2</sub>O from the benzaldehyde oxime. In all three cases, these intermediate hot spot products involve methyl group C—H bond rupture. A KDIE detonation study of TNT and TNT-d<sub>3</sub> shock initiated by an exploding foil method, demonstrates a small but positive KDIE ( $V_d/V_h > 1.00$ ) where the flyer plate velocity for the deuterium labeled compound is higher (Table XII).<sup>6</sup> While the indirect nature of this study does not permit a

KDIE ratio to be determined quantitatively, the appearance of a positive KDIE is significant and could be caused by the same rate-controlling C-H bond rupture<sup>6</sup> as that seen in the slow ambient pressure IDSC investigation<sup>1</sup> of TNT

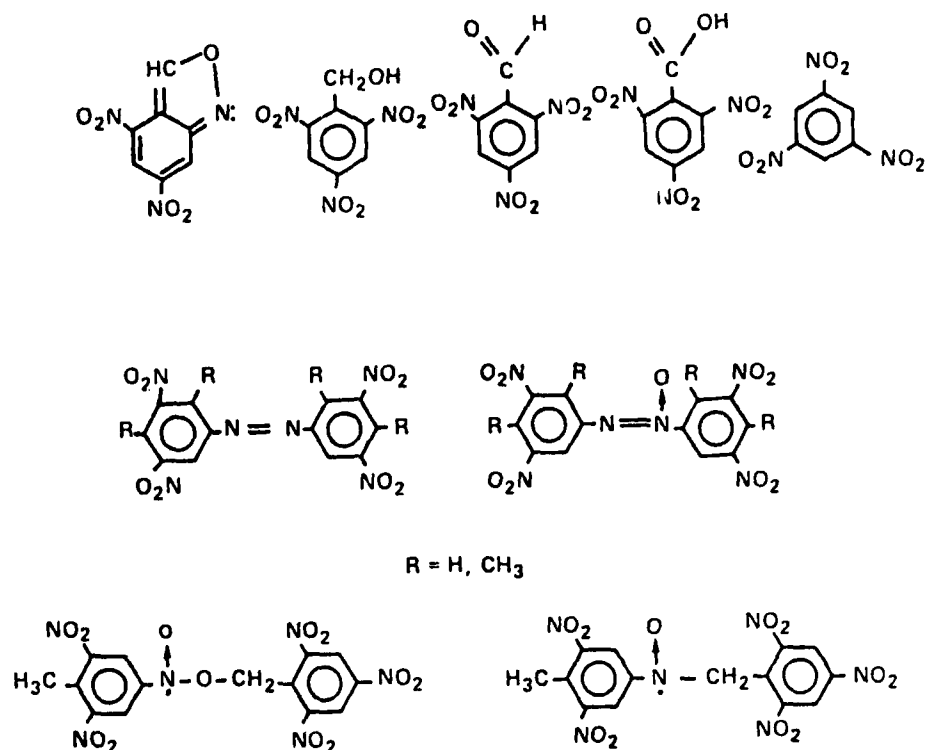


Figure 13. Isolated products and nitroxyl radical species from the TNT thermochemical decomposition process.<sup>1, 35, 36</sup>

Table XII. Exploding Foil Shock Detonation KDIE Values.<sup>6</sup>

| Sample               | Flyer Plate Vel.(mm/ $\mu\text{s}$ ) | Std Dev | KDIE Type                        |
|----------------------|--------------------------------------|---------|----------------------------------|
| TNT                  | 3.381                                | 0.127   |                                  |
| TNT                  | 3.237                                | 0.170   | Positive - i.e.                  |
| TNT-g-d <sub>3</sub> | 3.681                                | 0.155   | 1 <sup>0</sup> or 2 <sup>0</sup> |

and TNT-g-d<sub>3</sub>. When one considers both the products isolated from TNT in the sub-ignition impact study and the positive KDIE observed in the shock induced detonation study of TNT and TNT-d<sub>3</sub>, it is plausible that the same liquid state

TNT methyl group C-H bond rupture observed in the earlier KDIE condensed phase thermochemical decomposition process,<sup>1</sup> also constitutes the overall rate-controlling mechanistic step for these higher order incidents.

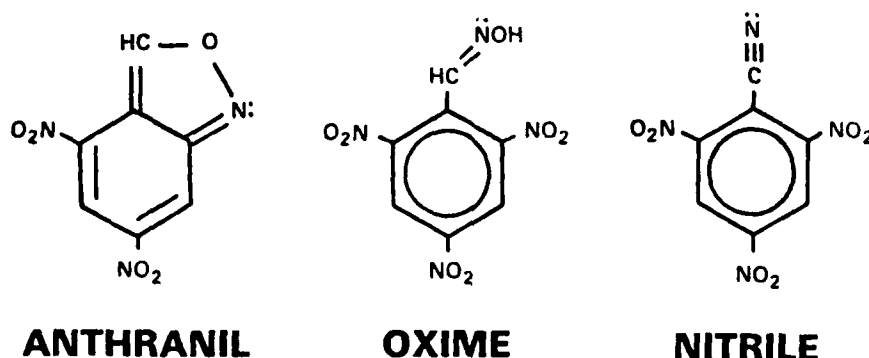


Figure 14. Products formed from sub-ignition of TNT by mechanical impact.<sup>31, 40</sup>

### 3. Conclusions

A review of various mechanistic investigations of both nitroaromatic (TNT, TATB) and nitramine (HMX, RDX) energetic compounds using the condensed phase kinetic deuterium isotope effect (KDIE) approach demonstrates a finite and significant degree of chemical kinetic control in all high energy incidents. Whether the high energy incident is a mild slow ambient pressure thermochemical decomposition process, a more rapid pyrolytic decomposition/deflagration process, a progressively more drastic higher pressure/temperature combustion, thermal explosion, or detonation event, discernable KDIE values appear with thermal, impact, or shock initiation methods. These KDIE values show rupture of the covalent C-H/C-D bond (N-H/N-D bond for TATB) or a bond in its immediate vicinity, generally constitutes the overall or global rate-controlling step of the high energy incident. In one case, the rate-controlling step apparently results from a thermal weakening of a solid compound's attractive intermolecular crystal lattice forces in the short-lived HMX mixed melt phase. When an energetic compound's rate-controlling mechanistic step may vary with different physical states as shown by HMX, the type of KDIE observed can strongly hint at the predominant physical state present during a given high energy incident; and in such a case, suggests the rate-controlling step controlling the global rate of energy release, may reside in the condensed phase process of high order events like combustion, thermal explosion or detonation. The condensed phase chemical processes, therefore, must be computationally modeled in order to develop acceptable computer codes that accurately predict energy releasing behavior. The presence of condensed phase products formed during these various high energy incidents by chemical pathways that are consistent with KDIE determined rate-controlling mechanistic steps, suggest the same rate-controlling step seen in the mild thermochemical decomposition process often mirrors those found in the

faster pyrolytic decomposition/deflagration process or in the progressively more drastic higher pressure/temperature/rate combustion, thermal explosion, detonation events. This apparent KDIE determined mechanistic relationship between the decomposition process and both combustion or explosion events suggests that condensed phase KDIE data obtained from the mild thermochemical decomposition process, can serve as a valuable guide in designing or planning mechanistic investigations of higher order energetic incidents, and that the condensed phase KDIE approach constitutes a valuable experimental tool for making mechanistic comparisons among them.

#### 4. Acknowledgements

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